Effects of Biopolymer as Drag Reducing Agent on Characteristics of Crude Oil

by

Muhamad Fauzan bin Abd Latif

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons.)
(Mechanical Engineering)

SEPTEMBER 2013

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CERTIFICATION OF APPROVAL

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Approved by,

_____

DR. AZURAIEN BINTI JAPPER @ JAAFAR

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for all the work that had been done and submitted in this project, that all the work done are my own except for the work that has been specified in the references and acknowledgement and that the original work contained here have not been undertaken or done by unspecified sources or persons.

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MUHAMAD FAUZAN BIN ABD LATIF

ABSTRACT

One of the important processes in retrieving oil is transportation of the oil from offshore to onshore facilities using pipelines. However presence of drag in the pipelines imposes various problems and one of them is increase in the pumping power needed in order to maintain constant flow rate throughout the pipelines. In order to reduce drag in pipelines, drag reducing agent (DRA) is introduced. Through years of researches, DRA is proven to be able to reduce drag in pipelines thus increases the crude oil's flow rate. However, DRA doesn't have an unlimited life. It will eventually break down with time and is needed to be disposed. Disposing DRA made of synthetic polymer is harmful to environment. Therefore, a natural DRA made from natural resources such as banana peel has been introduced. Presently, the knowledge on the effects of biopolymer as DRA on the characteristics of crude oil is limited. This project is conducted in order to further gain the knowledge on biopolymer DRA effects on the characteristics of crude oil. Biopolymer causes increase in wax appearance temperature both seeded and unseeded crude oil. Furthermore, the addition of biopolymer also cause incremental of pour point temperature of crude oil compared to the one without biopolymer. The carbon number distribution of the crude oil is also affected by the addition of biopolymer. Biopolymer causes the amount of compounds to increase but with different margins.

ACKNOWLEDGEMENT

First and foremost I would like to express my gratitude towards my supervisor, Dr. Azuraien Jaafar for she has always been encouraging and motivates me to complete the project. She often gives advices and guides me throughout the whole project in which would never be successful without her guidance. Her flawless communication and wide range of knowledge and experience has always made me feel comfortable to communicate with her.

Special gratitude for Ms. Harvin, Mr. Petrus, Mr. Abdourahman, Mr. Afnan, Mr. Jay, and Mr. Hazri as they often helps me with the project. Most of the times I get to engage with them as they have the knowledge and experience that are closely related to this project. They also made great colleagues and I would never hesitate to work together with them in the future.

Not to forget, a great appreciation to the Mechanical Engineering Department and Chemical Department of Universiti Teknologi PETRONAS for they have provided me with decent laboratory facilities that helps a lot in the completion of this project. The research officers and the technicians are also friendly and willing to offer help and advices for this project.

Last but not least, I would like to thank my family and friends as they never stop supporting me in any way they can from the start until the completion of my project.

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CHAPTER 1

INTRODUCTION

1.1. Background

Since the discovery of oil, lots of developments in various areas have been done in order to harvest the best out of the oil. These includes the development of new and better technologies and machineries to explore, retrieve the oil and to transport the oil retrieved to onshore facilities for refining of the oil so that useful products can be made out of it and be used by mankind. It is undeniable that oil really did great to us mankind. Transportation of the oil, like any other processes involved, is very crucial.

In real life, transporting the oil has its problems and challenges and one of them is drag. Drag causes pumping power loss that lead to pressure loss and pressure loss means reduction in flow rate of crude oil. Researchers worked had to find solutions to counter this problem and at one point, Drag Reducing Agent (DRA) has been discovered. DRA effectively reduce the drag in the pipelines thus increases the flow rate of crude oil. Commonly, most used DRA nowadays are made of synthetic polymer but due to the risks it imposes to the environment, researchers started to look for alternatives for synthetic polymer to make DRA and that is to use natural resources. One of the natural resources is banana peel. The biopolymer synthesized from banana peel effectively acts as a DRA in pipeline.

Despites the rapid development of biopolymer as DRA, the changes in the characteristic of crude oil when DRA is added should also be taken into account. This is very important to determine whether the biopolymer used could improve the characteristics of the crude oil or otherwise. Tests should be done to prove that biopolymer DRA helps to improve the characteristics of crude oil before it can be widely commercialized.

1.2. Problem Statement

As DRA was first commercialized for the usage in pipelines, it was made from synthetic polymer. DRA from synthetic polymer imposes risk when it comes to the disposal of used DRA. Later came the new version of DRA that was made from biopolymer; polymer synthesized using natural resources such as banana peel. The biopolymer produced was effectively used as DRA and increase the performance of crude oil flow rate.

As biopolymer DRA is used, the knowledge on its effects towards the characteristics of crude oil is limited due to the facts that it can be made from different natural resources and each of them might have different effects on the characteristics of crude oil such as wax appearance temperature, pour point temperature, carbon number distribution. One of the DRA is the one made from banana peel.

1.3. Objective

The sole objective of the project is to study the effects of biopolymer DRA on the characteristics of crude oil of different parameters.

1.4. Scope of Study

i. To study the characteristics of crude oil
ii. To study the procedures to conduct wax appearance temperature, pour point temperature and carbon number distribution tests.
iii. To conduct aforementioned tests using crude oil seeded and unseeded with drilling mud and with and without biopolymer added into the samples.

CHAPTER 2

LITERATURE REVIEW

2.1. History and formation of oil and natural gas

Modern history shows that, the first modern oil well is drilled in Asia, on the Aspheron Peninsula north-east of Baku. Naturally occurring gas modern history dated back to as early as 1626, when French explorers discovered American natives igniting gases that were seeping into and around Lake Erie. Now that we know when the oil and the natural gas were first time discovered, we might also want to know about how they are formed. As stated in "Oil",(1919), "Diagenesis is a process of compaction under mild conditions of temperature and pressure. When organic aquatic sediments (proteins, lipids, carbohydrates) are deposited, they are very saturated with water and rich in minerals. Through chemical reaction, compaction, and microbial action during burial, water is forced out and proteins and carbohydrates break down to form new structures that comprise a waxy material known as 'kerogen' and a black tar like substance called 'bitumen'. All of this occurs within the first several hundred meters of burial. The bitumen comprises the heaviest components of oil, but the kerogen will undergo further change to make hydrocarbons" explains the first phase of oil formation through Diagenesis. Figure 2.1 depicts formation of oil.

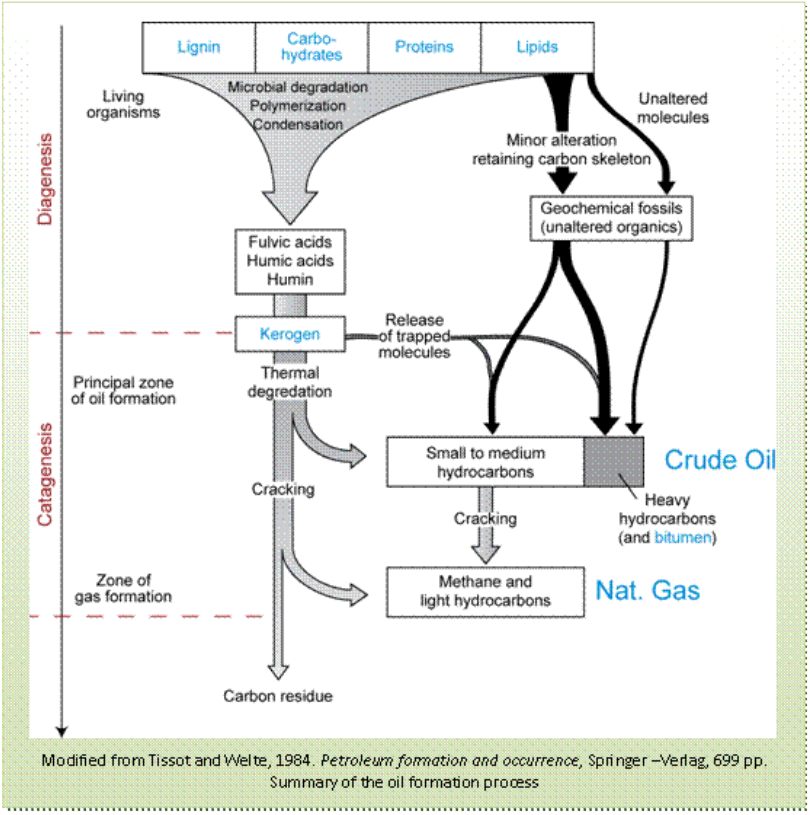


Figure 2.1: Formation of crude oil extracted from http://www.ems.psu.edu/~pisupati/ACSOutreach/Oil_2.html

As these sediments are buried deeper and deeper as more new layers are formed over it, second phase will occur where catagenesis or cracking will turn kerogen into oil and natural gas. The article also stated that temperature and pressure increases with depth and catagenesis, will took place. Certain conditions of catagenesis will leads to different products where higher temperature and pressure will cause a more complete cracking that turns the kerogen into lighter, smaller hydrocarbon and oil formation have a specific window of conditions. These conditions will determine whether the kerogen will become natural gas or remain as trapped kerogen. From the article it is understood that there are specific parameters required that will cause the kerogen to either stay as kerogen, or become natural gas, or oil.

2.2. Turbulent in pipeline

Since the drag reduction phenomenon was first discovered by Tom in 1948, most of the research areas were focused on the synthetic polymer DRA. For this project, the author tried to explore on a more specific and less explored side of DRA polymer which is natural polymer. But first, the concept of fluid flow in pipes must be understood. As suggested by Toms, polymer solution flow in a pipe require much lower pressure gradient to maintain the same amount of flow rate compare to the solvent alone. This means, when water flow is mixed with the natural polymer as DRA, with the same pump operating pressure, higher flow rate can be obtained compared to the water flow alone with no natural polymer DRA in the pipe.

Cengal and John (2006) in their article state that fluid flow can be described into 2 main behavior s which is laminar flow and turbulent flow. In laminar flow, the fluid flow in a uniform manner. Dye streak that is injected into the flow produced a smooth and straight line in laminar region. In contrast, dye streak will form random zig zag motion in turbulent flow. In turbulent flow, the fluid is flowing in highly disorder or chaotic manner. The transformation between laminar flow into turbulent flow is called transition state. Figure 2.2 shows the side view of laminar and turbulent flow in a pipeline.

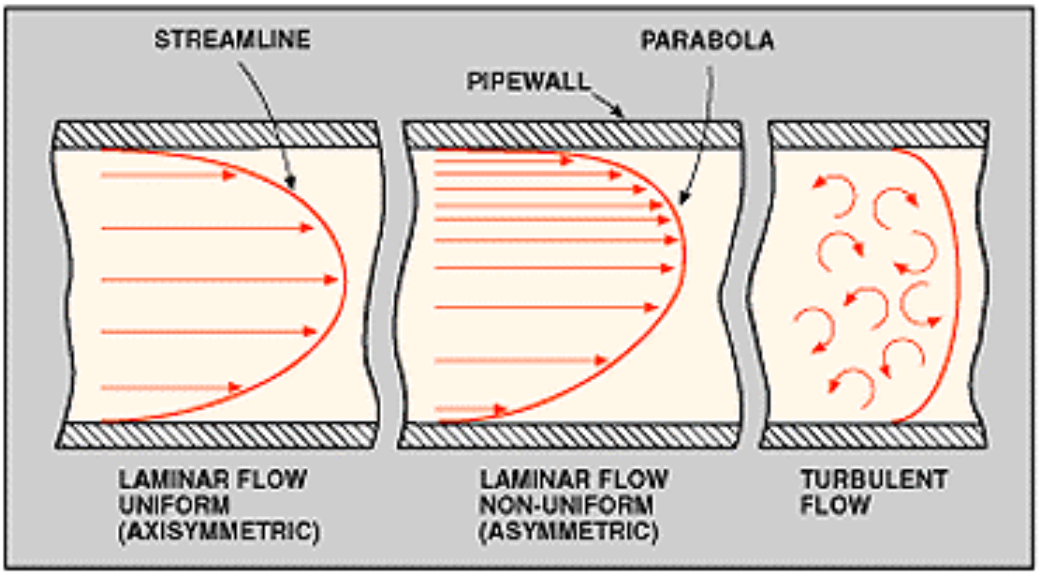


Figure 2.2 : Laminar flow and turbulence flow in a pipeline side view extracted from http://www.omega.com/techref/flowcontrol.html

During the fluid flow, not all fluid particles travel at the same velocity within a pipe. The fluid velocity in a pipe changes from zero at the inner wall surface to maximum at the center of the pipe. The fluid velocity is zero at the wall due to no-slip condition and the velocity must be highest at the center to keep mass flow rate.

The shape of the velocity curve, which is represented in the velocity profile across any given section of the pipe, depends upon whether the flow is laminar or turbulent. If the flow in a pipe is laminar, the velocity distribution at a cross section will be parabolic in shape with the maximum velocity at the center being about twice the average velocity in the pipe. In turbulent flow, a fairly flat velocity distribution exists across the section of pipe. Figure 2.3 below illustrates the above theory of velocity profile in the pipe.

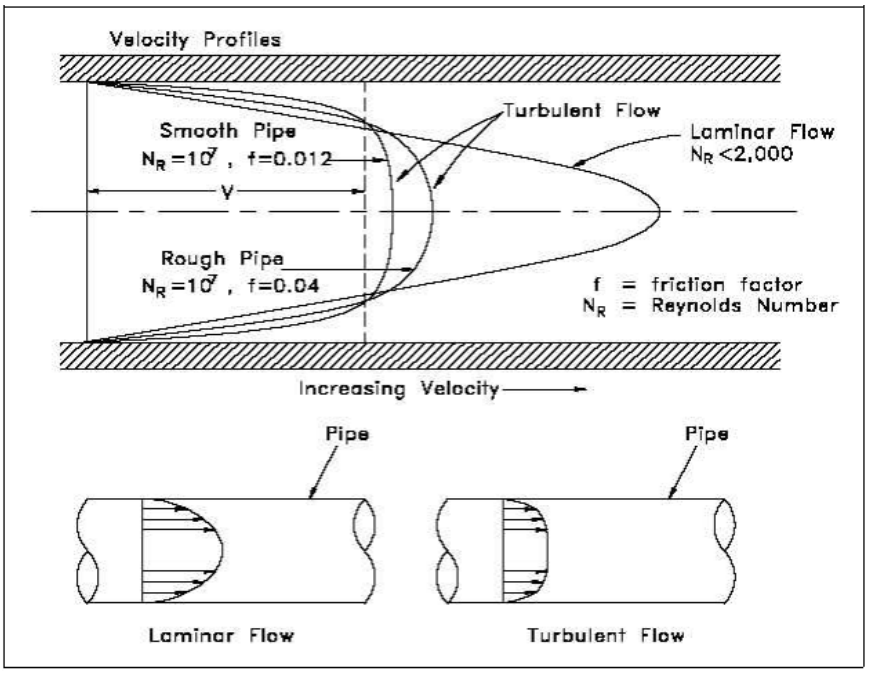


Figure 2.3 : Laminar and turbulent flow velocity profile extracted from http://nuclearpowertraining.tpub.com/h1012v3/css/h1012v3_40.htm

Characterized by the distance to the wall, Cengel and John (2006) classified velocity profile in turbulent region into a few regions. The very thin layer next to the wall where viscous effect is dominant is the viscous sub layer. Next to the viscous sub layer is the buffer layer, in which turbulent effect is significant, but the flow is still dominated by the viscous effect. Above the buffer layer is the overlap layer in which turbulent effect is significant. Above this layer is turbulent layer and the turbulent

effect is much more significant compare to the overlap layer. Some literature classified these layers with other names.

The flow behavior can be distinguished based on the Reynolds number. Reynolds number is given as the ratio between inertial forces and viscous forces and flow behavior is dependent on which forces are more dominant.

Equation 1: Reynolds Number,

$$Re = \frac{\boldsymbol{inertial\ forces}}{\boldsymbol{viscous\ forces}}$$

Dominant inertial force resulting in laminar flow and turbulent if the viscous tend to be dominant. Under most practical condition, fluid behaviors are classified according to following value of Reynolds number.

$Re < 2300$ laminar flow

$2300 < Re < 4000$ transitional flow

$Re > 4000$ turbulent flow

Two regions will be formed inside the pipe which is entrance region and fully developed region. In hydrodynamic entrance region, the velocity profile of the fluid is being developed. After a certain distance from the entrance of pipe, the velocity profile will become constant and this region is known as hydrodynamically fully developed region. Velocity profile in the fully developed laminar flow has a parabolic shape and somewhat flatter in fully developed turbulent flow.

Escudier and Smith (1999) describe that turbulent flow is characterized by random and a rapid fluctuation of swirling region of fluid called eddies, throughout the flow. In turbulent flow, the swirling eddies transport mass, momentum and energy to other region of flow much more rapidly compared to laminar flow. In the study, it is observed that the viscous sub layer plays a passive role in drag reduction effect. However the buffer zone and logarithmic layer are considerably affected. The buffer zone increases in thickness with increasing level of drag reduction. This results in high flow velocity in logarithmic layer, which is responsible for the increase in the flow rate with the introduction of drag reducing polymer.

As the mechanism involved, the drag reduction phenomenon is the attribute to the shear waves caused by the elasticity of polymer chain. This shear waves are thought to suppress the turbulent velocity fluctuations at small scales thereby reducing the viscous drag. In recent experimental work, it has been shown that turbulent shear stresses are substantially suppressed by polymer chain. This study revealed that unraveling of polymer chains is indeed an essential ingredient in the ability of a polymer to reduce viscous drag.

2.3. Drag reduction in pipeline using polymer DRA

Liquids in pipeline, especially water, crude oils, product of refinery, are always being transported under turbulent flow in a pipeline. Because of this turbulent structure in flow media, severe amount of drag of flow will be created along the pipeline. As a result, there will be a lot of pressure loss during the transportation and higher pumping power will be needed to make sure liquid can reach the destination (Mashelkar, Kale, & Ulbrecht, 1975).

Through research over the years, it is found that one of the solutions to pumping power losses during liquid transportation flow is using additive (soluble chemical) to the main flow. Toms (1948) was the first author who described the effect on flow of the addition of a small amount of high molecular weight polymers to a liquid, which phenomenon was called ‘drag reduction’.

One of the most impressive successes in polymer applications for drag reduction was the use of 10ppm oil-soluble polymers in the trans-Alaska pipeline system which increased pipeline flow rates significantly (Burger, Munk, & Wahl, 1982). Actually in oil industry, oil soluble and long-chain polymers had been identified as the effective chemical to reduce the frictional pressure drop caused by turbulence in a pipeline. The operating pressure can be reduced while keeping the same flow rate or the throughput can be increased while applying the same pressure.

To evaluate more about the mechanism of the DRA, Sedahmed et al. (1984) found that polymer molecules are assumed to undergo a dynamic chain elongation that interacts with the eddies in the flow, altering the whole energy balance of the turbulence. This chain stretching occurs under high shear and explains why drag reduction is generally accepted as near-wall phenomenon. As the action of the

polymer mainly located at the near-wall region, only a few tens of parts per million by weight of product are required. The low concentrations make polymer chemicals economically attractive. They are all easier to handle and are known to reduce the effect of diffusion controlled corrosion.

2.4. Biopolymer

Banana peel is one of the natural resources to synthesize biopolymer. As banana peel represents 40% of total weight of the fruit (Tchobanoglous et al., 1993), it is considered to be underutilized. Normally the fruit will be eaten and the peel will be thrown away. In order to utilize it, one of the best ways is to convert it into Carboxymethylcellulose so that it can be used as drag reducing agent. Using proximate composition of banana peels, Cavendish green peel is chosen as the source of Carboxymethylcellulose as it has content of carbohydrate and crude fiber which will result in more Carboxymethylcellulose.

Carboxymethylcellulose is an environmentally friendly, modified polymer made from cellulose. Cellulose is available vastly as it can be found in wide range of sources such as the wood and agriculture waste. However banana peel is chosen as it is available all year round.

2.5. Characteristics of crude oil

However, there are limited studies on the effect of biopolymer as DRA on the characteristics of crude oil. Some of the characteristics that are significant to be considered during the transportation are Wax appearance temperature (WAT), Pour point temperature and carbon number distribution. By knowing the effects of biopolymer DRA towards crude oil, we are able to maintain the quality of crude oil during transportation of it.

“Pour point”,(2013) defines that WAT as the temperature at which wax crystals first start to form in a crude oil. Wax appearance temperature (WAT) and wax precipitation temperature (WPT) are other synonym for the wax appearance temperature. Cloud point also is another synonym for WAT. Mustafa V et al (1996) stated that WAT is a temperature point when crystallization is visible. As the crude oil pass to a point of low temperature, wax crystal started to form (“Cloud

point,"2013). Wax crystal then grow and later covers the inner wall of the pipeline. Slowly, the thickness of wax increases then causes the pressure across the pipe to drop. This leads to higher pumping power needed to maintain the flow rate. However this problem can be controlled by insulation and heating of the pipe to a temperature above its cloud point ("Paraffin / Wax and Waxy Crude Oil," 2013). Figure 2.4 illustrates the formation of crystal structure as the temperature goes down.

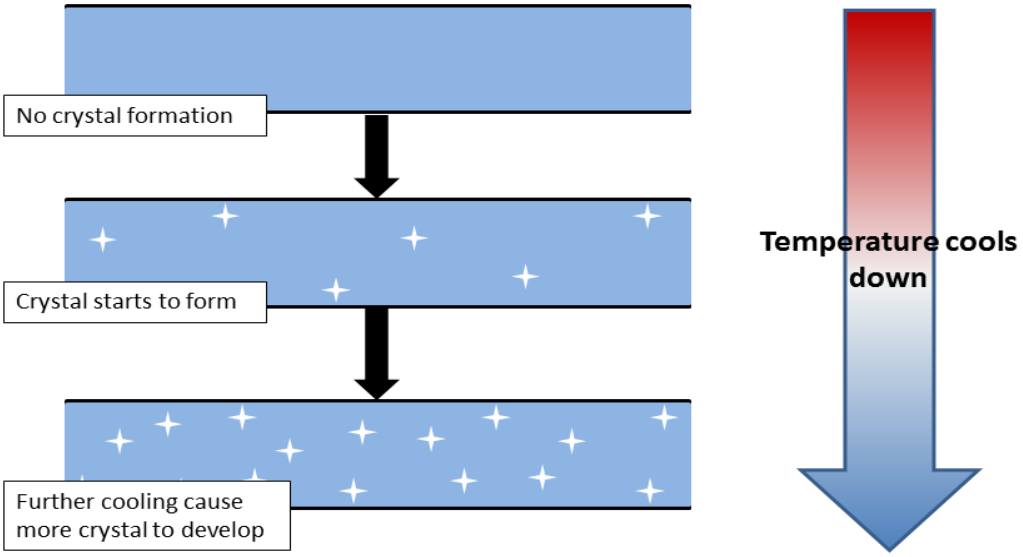


Figure 2.4: Formation of crystal in crude oil

"Pour point",(2013) also stated that pour point temperature is the temperature point in which a liquid ceases to pour (does not behave like a fluid). As temperature decreases, oil will also started to become more viscous and behave like a fluid lesser and lesser until at one point the oil does not behave like a fluid anymore and it will stop flowing. The pour point of waxy crude oil depends on the amount of wax, the crystallization habit of the wax and the shear stability of different wax structure (Tiwary and Mehrota, 2002). In conclusion, the pour point of a waxy crude oil is lower than the wax appearance temperature of the crude oil.

2.6. Carbon number distribution

Commonly found molecules in petroleum hydrocarbon are alkanes, cycloalkanes, aromatic hydrocarbons and asphaltenes. The composition and condition of crude oils are different from one reservoir to another and gas chromatograph is used to analyze the composition of gas and liquid of a crude oil.

The hydrocarbons that contain heteroatoms could vary from very simple one such as thiophene to very complex mixtures such as asphaltenes for which the structure is not well understood, but known to contain sulfur, oxygen and nitrogen at different levels, in addition to carbon and hydrogen (Buenrostro-Gonzalez *et al*., 2002; Woods *et al*., 2008)

Petroleum fraction can be generally divided into two; light fraction and heavy fraction, where the light fraction consists of alkanes and aromatics while the heavy fraction consists of saturates, aromatics, resins and asphaltenes fraction. This fraction can be determined using Gas Chromatograph however is limited due to high boiling point of Resins and Asphaltenes.

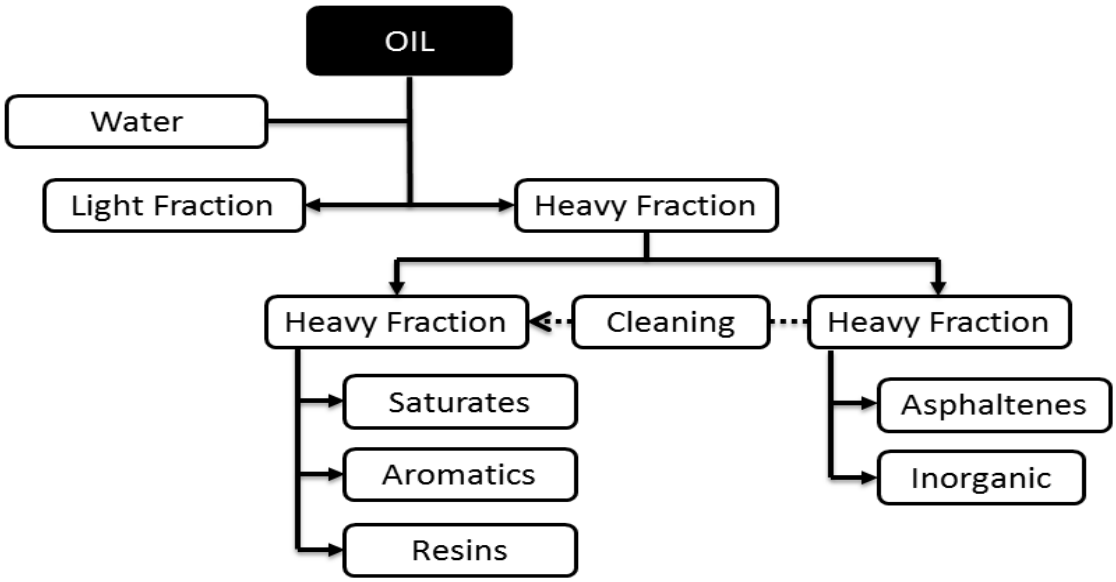


Figure 2.5: Flow chart of fractionation of Crude oil

CHAPTER 3

METHODOLOGY

Following methods are to be adapted throughout the project. Figure 3.1 shows the flow chart used for the project. Flow chart is constructed first as this will greatly help to maintain the track of the project's progress.

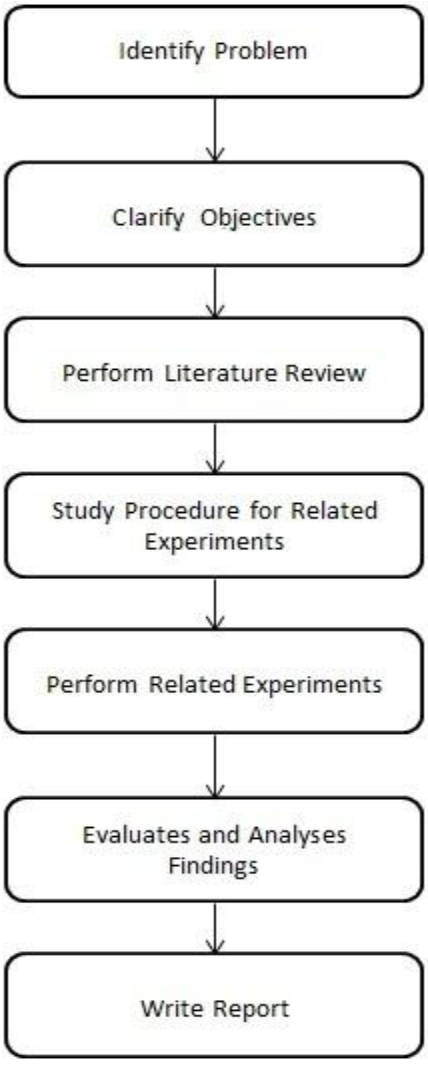


Figure 3.1: Final year project flow chart

3.1. Reading Materials

There are many online materials that can be found that are related to this project. Research papers, technical papers, journals and articles that are related can be found with the help of search engine such as Google. All these materials are from different and reliable sources.

However there are no textbook found yet as there are almost no textbook on flow assurance. Yet the author did find textbooks that help him to understand the basics of fluid dynamic. With all the related articles that the author found, the author spend at least an hour every day to read and study the materials.

3.2. Consultation

Every week, the author tries to find slots to meet with his supervisor for consultation session. However most of the time the author will work closely with the appointed personnel as they are easier to reach and met. Email also works as a medium for the author to consult if he wasn't able to meet his supervisor or the appointed personnel.

Furthermore the author also participates in engineering forum and asks related questions to the author's project. The forum not only has student as members but also engineers too. The answers and opinions given by the community of the forum have also helped the author to complete this project.

3.3. Project Activities

There are several tests that have been carried out in order to study the effects of biopolymers as DRA on the characteristics of crude oil.

Before carrying out any of the activities, Health and Safety matters should be a priority. Since Sepat7 contain traces of sulphur and mercury, safety measures must be taken during handling of it.

Personal protective equipment (PPE) should be worn. Lab coat, fully covered shoes, protective eyewear, disposable respirator and latex glove are the ppe used during any of the activities. Furthermore, mixing and heating of the samples should be carried out in fume hood. Figure 3.2 below shows the experimental setup for crude oil, drilling mud and biopolymer mixing.

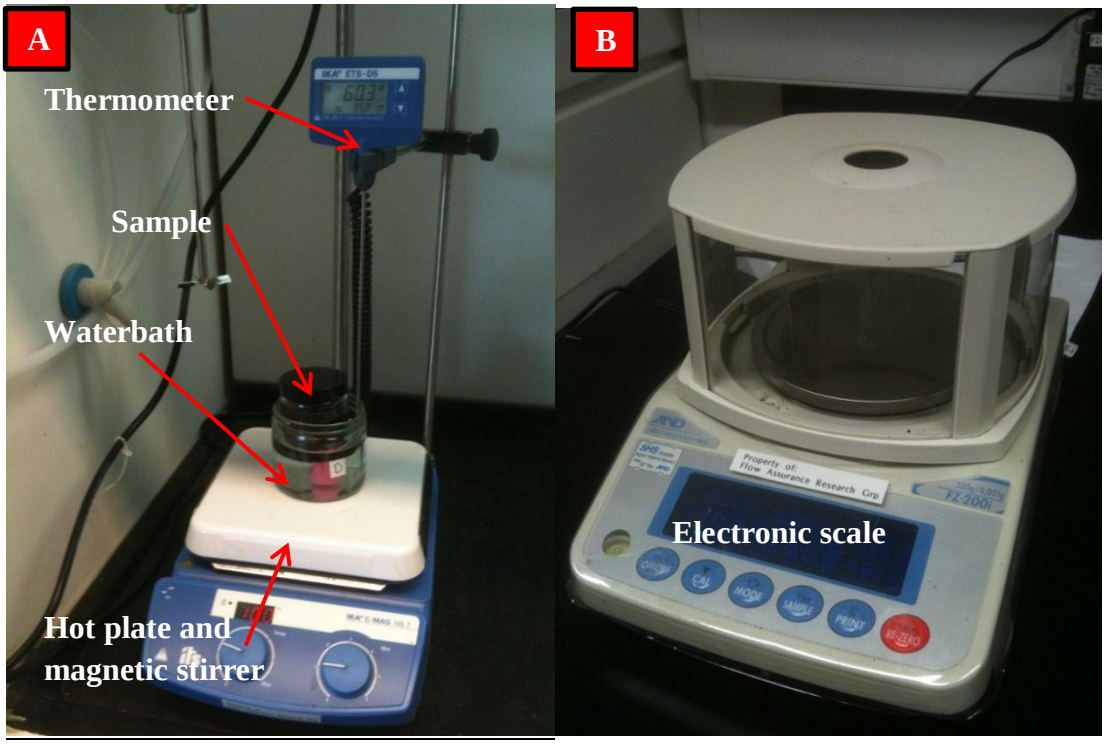


Figure 3.2: Crude oil, drilling mud and biopolymer mixing experimental set up. A) Hot plate with magnetic stirrer, thermometer and water bath. B) Electronic weight scale.

3.3.1. Crude Oil Mixing

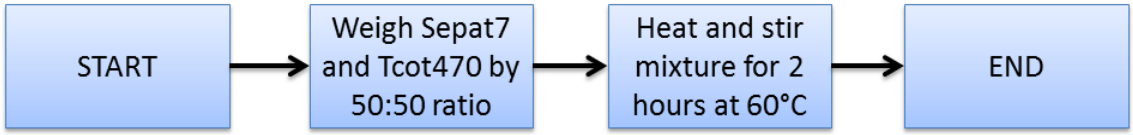


Figure 3.3: Crude oil mixing flow chart

Sepat 7 crude oil is too waxy, thus it is needed to be mixed with crude oil from other field in order to reduce its waxiness. This is so that the samples can be tested with DRA in the double concentric cylinder under the rheometer. As for this project, TcotP470 will be used to be mixed with Sepat 7 crude oil by 50:50 weight ratios. The mixing procedure is as follows:

1. Sample is prepared by weigh 50% Sepat7 and 50% TcotP470. For example to prepare 100g of mixture, weigh 50g Sepat7 and 50g TcotP470.
2. The sample is then heated in a water bath with a temperature of about 60°C (above WAT).
3. As the temperature reach 60°C, the sample is mixed using stirrer while maintaining the water bath's temperature for 2 hours.
4. When the mixing is done, sample is transferred into proper container and the container was labeled.
5. Before starting any experiment, the sample is needed to be heated in water bath so that is does not stay in waxy form.

3.3.2. Drilling Mud Mixing

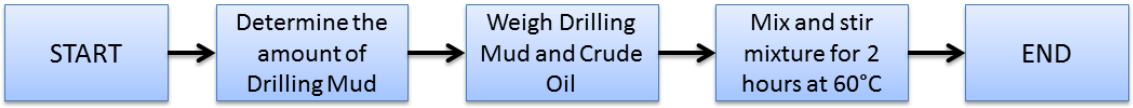


Figure 3.4: Drilling mud mixing flow chart

First the amount of drilling mud to be mixed needed to be known first. For this project, w/w% is used as it is easier to measure compared to using v/v%. Using 100g as the amount of product, use the following calculation to determine the amount of drilling mud.

For 3% Drilling Mud (w/w%)

Xoil (g) + Xmud (g) = 100g

$$\frac{\boldsymbol{Xmud}}{\boldsymbol{Xmud+Xoil}} = \frac{\mathbf{3}}{\mathbf{100}}$$

$$\mathbf{100}(\boldsymbol{Xmud}) = \mathbf{3}(\mathbf{100}\boldsymbol{g})$$

$$\boldsymbol{Xmud} = \frac{\mathbf{3}(\mathbf{100}\boldsymbol{g})}{\mathbf{100}} \#$$

$$\boldsymbol{Xmud} = \mathbf{3}\boldsymbol{g}$$

$$\boldsymbol{Xmud} + \boldsymbol{Xoil} = \mathbf{100}\boldsymbol{g}$$

$$\boldsymbol{Xoil} = \mathbf{100}\boldsymbol{g} - \mathbf{3}\boldsymbol{g}$$

$$\boldsymbol{Xoil} = \mathbf{97}\boldsymbol{g} \#$$

Thus for 100g product, the amount of mixture for 3 % DM is 97g crude oil mixture and 3g drilling mud.

For 9% Drilling Mud (w/w%)

Xoil (g) + Xmud (g) = 100g

$$\frac{\boldsymbol{Xmud}}{\boldsymbol{Xmud+Xoil}} = \frac{\mathbf{9}}{\mathbf{100}}$$

$$\mathbf{100}(\boldsymbol{Xmud}) = \mathbf{9}(\mathbf{100}\boldsymbol{g})$$

$$\boldsymbol{Xmud} = \frac{\mathbf{9}(\mathbf{100}\boldsymbol{g})}{\mathbf{100}}$$

$$\boldsymbol{Xmud} = \mathbf{9}\boldsymbol{g}\ \#$$

$$\boldsymbol{Xmud} + \boldsymbol{Xoil} = \mathbf{100}\boldsymbol{g}$$

$$\boldsymbol{Xoil} = \mathbf{100}\boldsymbol{g} - \mathbf{9}\boldsymbol{g}$$

$$\boldsymbol{Xoil} = \mathbf{91}\boldsymbol{g}\ \#$$

Thus for a product of 100g, the amount of mixture for 9% DM is 91g crude oil mixture and 9g drilling mud.

The mixing procedures are as follows:

For 3% Drilling Mud

1. Drilling mud is heated in water bath for about 10 minutes.
2. For 3% drilling mud, 3g of drilling mud is weighed.
3. 97g of Crude oil is heated in water bath at 60°C.
4. As the temperature of crude oil mixture is nearly 60°C, weighed drilling mud is immediately added and it is stirred using stirrer for 2 hours.
5. When the mixing is done, the sample is stored in suitable container and the container is labeled.

For 9% Drilling Mud

1. Drilling mud is heated in water bath for about 10 minutes.
2. For 9% drilling mud, 9g of drilling mud is weighed.
3. 91g of Crude oil is heated in water bath at 60°C.
4. As the temperature of crude oil mixture is nearly 60°C, weighed drilling mud is immediately added and it is stirred using stirrer for 2 hours.
5. When the mixing is done, the sample is stored in suitable container and the container is labeled.

3.3.3. Biopolymer Mixing

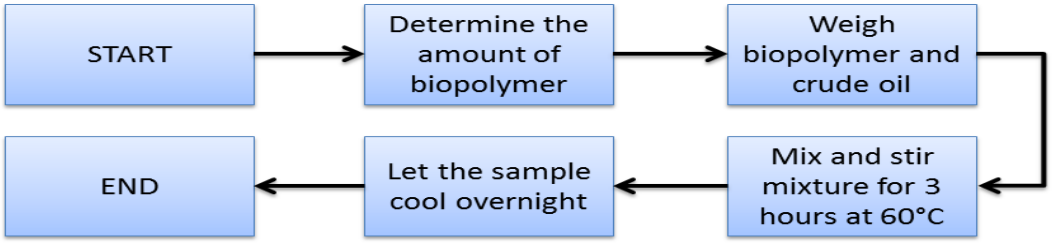


Figure 3.5: Biopolymer mixing flow chart

The right amount of biopolymer to be mixed with samples needed to be determined first. Assuming the amount of product is 100 gram; use the following calculations to determine the amount of biopolymer.

Standard requires 100ppm of biopolymer in the sample. Thus:

$$\frac{x}{x+y} = \frac{0.01}{100}$$

Since Y is the mass off crude oil, 100g.

$$\frac{x}{x+100g} = \frac{0.01}{100} = 1 \times 10^{-4}$$

$$x = (1 \times 10^{-4}) \times (x + 100g)$$

$$x(1 - 1 \times 10^{-4}) = 1 \times 10^{-4} \times 100g$$

$$x = 0.01g \#$$

For each 100g sample, 0.01g of biopolymer is added. The procedure is as follows:

1. Sample is heated in the water bath of 60°C (above WAT) until it is homogeneously mixed.
2. 0.01g of biopolymer is weighed using the electronic scale.
3. Biopolymer is then added into the heated sample and the mixture is stirred for 3 hours while maintaining the water bath's temperature at 60°C.
4. When the mixing is done, the mixture is stored in proper container and left overnight before using it for any experiment.

3.3.4. Wax Appearance Temperature

For wax appearance temperature, Rheometer AR-G2 is used. Figure 3.6 below shows the Rheometer set up.

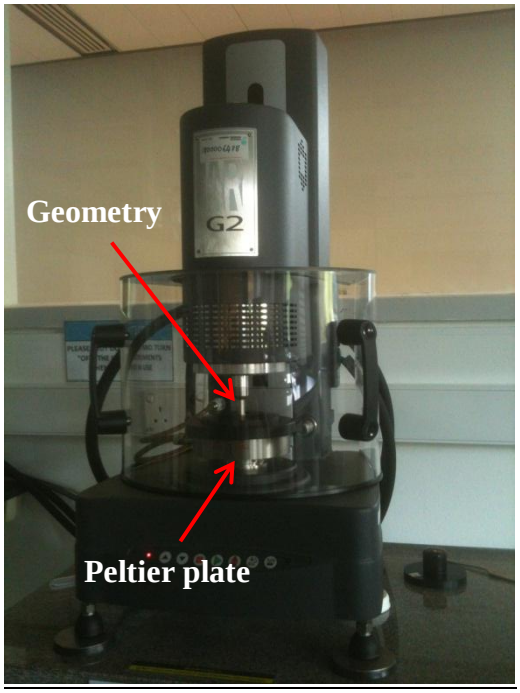


Figure 3.6: Rheometer set up

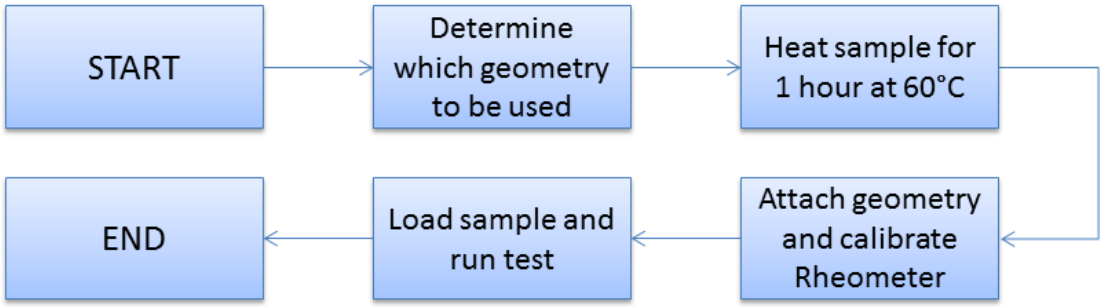


Figure 3.7: Wax appearance temperature using Rheometer flow chart

Rheometer is an instrument used to study the rheological properties of sample. This is a highly sensitive instrument which only certified or trained person can be allowed to operate the rheometer. Any breakdown will also take long time to fix the problem and it is costly.

Please take note that the following procedure needed to be fully understood first before it is carried out with precision.

Rheometer preparation:

1. The air compressor is turned on to supply air to the Rheometer.
2. Since the Rheometer is equipped with Peltier control device, the Thermo Cube which supply the water is turned on
3. The bearing lock is remove and then the power supply of Rheometer is turned on
4. TA Rheology Advantage is started up to check the communication between the computer and the instrument.

Running the test:

1. The chosen Geometry is attached and locked.
2. Mapping is started followed by Geometry Inertia calibration and Zero Gap calibration.
3. Most suitable procedure is chosen in TA Rheology Advantage. If there is no suitable procedure, new procedure is created.
4. Sample is loaded and the test is started.
5. Repeat step 1-4 with other samples.

WAT Rheometer Procedure

i) Conditioning Step 1

Initial Temperature	50°C
Wait for correct temperature	✓

ii) Peak Hold Step 1

Hold	Shear Rate (1/s)
At	10.00
Duration	0:02:00
Delay time	0:00:10
Temperature	50°C

iii) Conditioning Step 2

Initial Temperature	25°C
Wait for correct temperature	✓
Perform Equilibration	✓
Duration	0:02:00

iv) Temperature Ramp Step 1- Oscillatory

Temperature	50°C	15°C
Equilibration Time	0:01:00	
Ramp Time (°C /min)	1:00	
Delay time	0:00:10	
Controlled Variable (%strain)	0.01	
Angular Frequency (rad/s)	5.00	

v) Conditioning Step 3

Initial Temperature	50°C
Wait for correct temperature	✓

vi) Peak Hold Step 2- remove shear history

Hold	Shear rate (1/s)
At	10.00
Duration	0:02:00
Sampling Delay time	0:00:10
Temperature	50°C

vii) Conditioning Step 4

Initail temperature	25°C
Wait for correct temperature	✓
Perform Equilibration	✓
Duration	0:02:00

viii) Temperature Ramp Step 2

Temperature	50°C	15°C
Ramp Time (°C /min)	1:00	
Sampling Delay time	0:00:10	
Controlled Variable (Shear Rate)	10.00	

ix) Conditioning Step 5

Initial Temperature	50°C
Wait for correct temperature	✓

x) Peak Hold Step 3 – remove shear history

Hold	Shear rate (1/s)
At	10.00
Duration	0:02:00
Sampling delay time	0:00:10
Temperature	50°C

xi) Conditioning Step 6

Initail temperature	25°C
Wait for correct temperature	✓
Perform Equilibration	✓
Equilibration Duration	0:02:00

xii) Temperature Ramp Step 3- oscillatory to the recoverability

Temperature	50°C	15°C
Equilibration Time	0:01:00	
Ramp Time (°C /min)	1:00	
Delay time	0:00:10	
Controlled Variable (%strain)	0.01	
Angular Frequency (rad/s)	5.00	

xiii) Post Experiment Step

Set Temperature	✓
Temperature	45°C

3.3.5. Pour Point Test

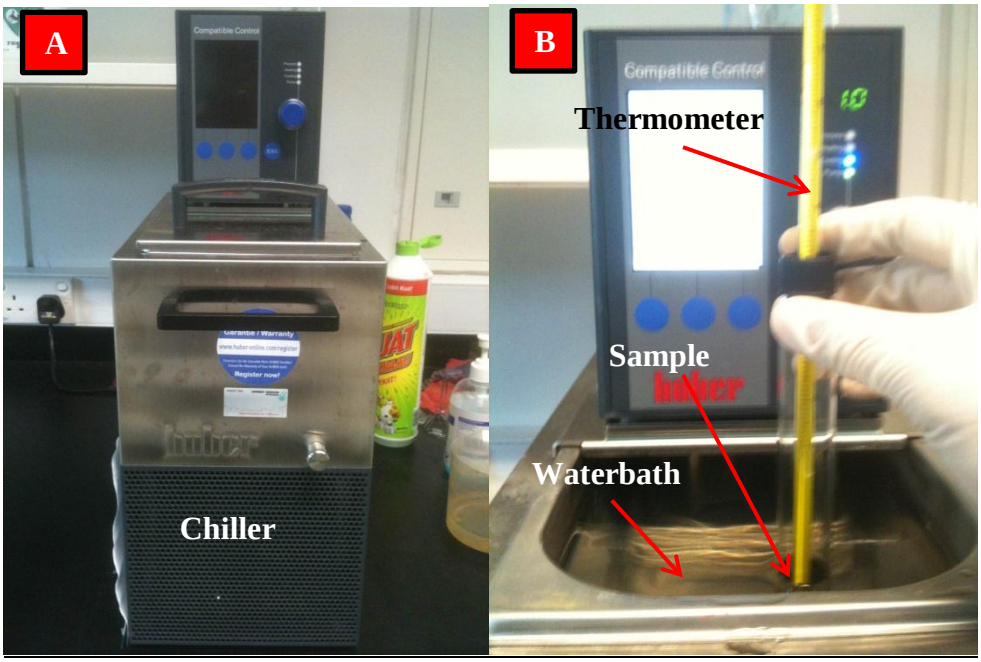


Figure 3.8: Experimental set up for pour point test

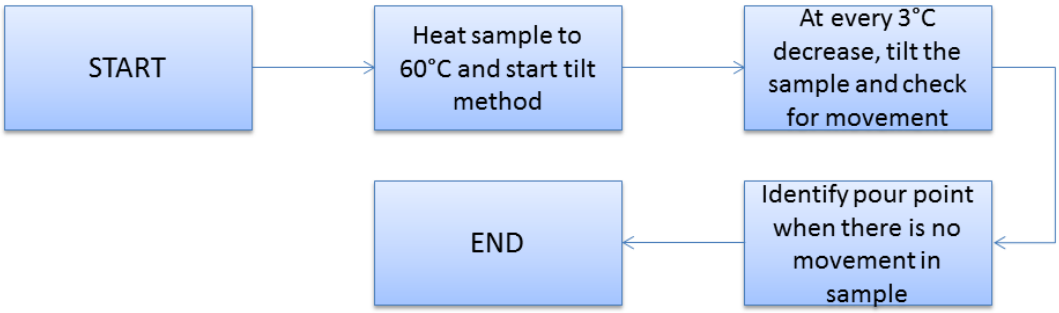


Figure 3.9: Pour point test flow chart

The pour point test setup and procedure is based on standard ASTM 5853 – Standard Test Method for Pour Point of Crude Oil. Since the pour point of each samples are not known, each sample is pre-heated to the maximum temperature of 60°C and is let to cool for 24 hours before Pour Point Test can be conducted.

The pour point test procedure is as follows:

1. The sample is transferred into test tube with thermometer.
2. The sample is immersed in hot water bath until it reached 45°C. Then the sample is immersed in cool water bath.
3. At each 3°C interval, the sample is taken out of the water bath and tilted horizontally to observe for any movement of the sample.
4. Step 3 is repeated until there is no movement detected.
5. Step 2 to 4 is repeated 3 times.
6. Step 1 to 5 is repeated with the remaining samples.

However this is not particularly accurate. Changes in the procedure have been made in order to increase the accuracy of this method.

1. The sample is transferred into test tube with thermometer.
2. The sample is immersed in hot water bath until it reached 45°C. Then the sample is immersed in cool water bath.
3. At each 3°C interval, the sample is taken out of the water bath and tilted horizontally to observe for any movement of the sample.
4. **At 3°C above expected pour point, the sample is taken out of water bath and tilted horizontally at each 1°C interval.**
5. Step 4 is repeated until there is no movement detected.
6. Step 2 to 5 is repeated 3 times.
7. Step 1 to 6 is repeated with the remaining samples.

3.3.6. Carbon Number Distribution

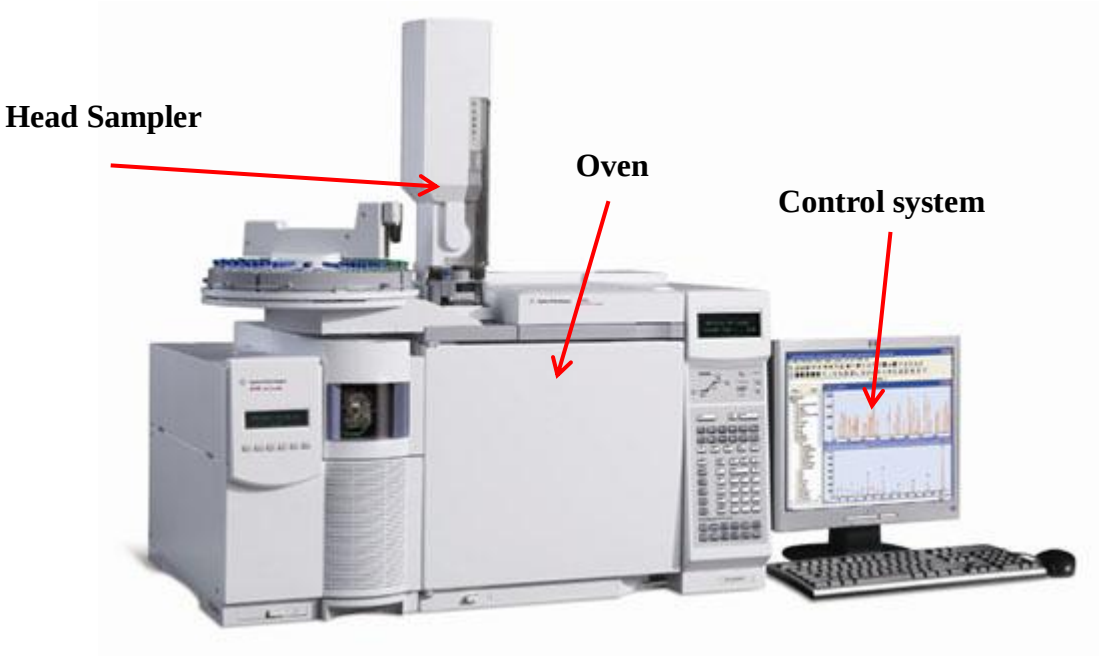


Figure 3.10: Gas Chromatography with auto head sampler

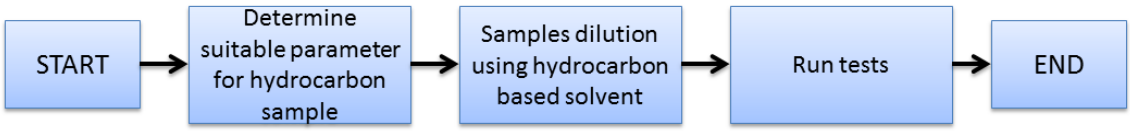


Figure 3.11: Carbon number distribution flow chart

Carbon number distribution can be determined using gas chromatography

1. The GS is turned on.
2. The sample is heated in water bath
3. Glass syringe and acetone is obtained.
4. GC is prepared for data collection and set to the following values:

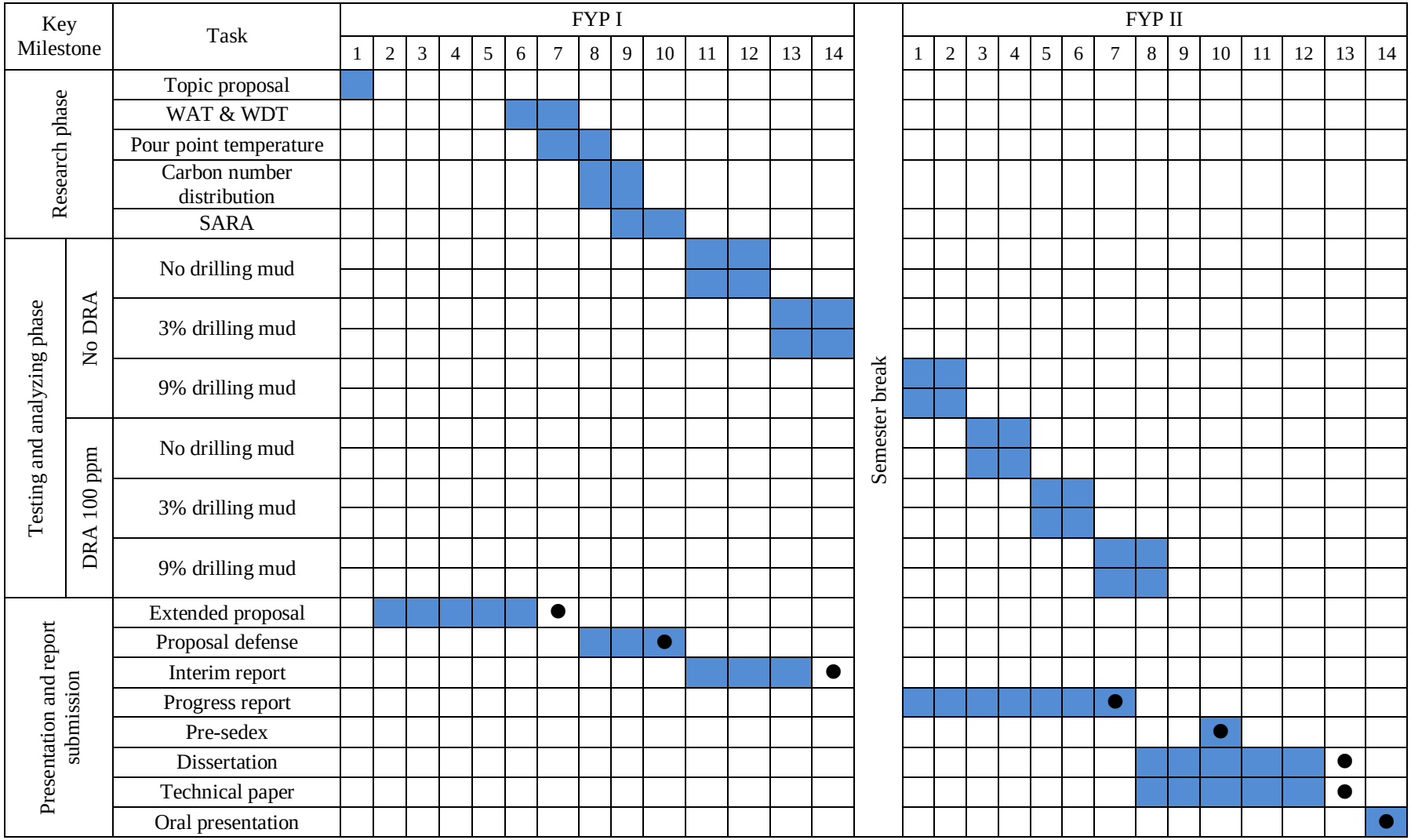
Table 3.1: Gas Chromatography parameter values

Start temperature	40°C
Hold time	5 min
Ramp time	5°C/min
Final temperature	300°C
Hold time	30 min

5. During GC warm up, following steps are used to clean the syringe.
    a. Plunger is fully depressed.
    b. Tip of syringe needle is submerged into vial of acetone.
    c. The plunger is pulled back until 1/3 of the barrel is filled with acetone.
    d. The content is expelled to Kimwipe of paper towel.
    e. Step a-d are repeated two times.
6. Step 5 is repeated to clean and flush the syringe with the gas collected from the container that contains the heated sample.
7. Gas from the heated sample is collected and prepared for injection.
    a. As GC is warmed up, using one hand to hold the syringe and another to steady the needle, it is inserted into the injection port until it is fully seated.
    b. Simultaneously, the plunger is depressed while the data is collected. The needle is pulled out immediately.
8. While data is collected, the syringe is flushed using step 5 a few times until syringe can move smoothly.
9. As data collection ended, chromatogram is analyzed.
10. Step 7-9 are repeated with the remaining samples.
11. GC is turned off when the final data collection is done.

3.4. Gantt chart

Table 3.2: Final Year Project Gantt Chart



CHAPTER 4

RESULTS & DISCUSSIONS

In this section, author will discuss the results and the findings of the experiment on wax appearance temperature, pour point temperature and carbon number distribution. During this project, all 6 samples used were labeled as A, B, C, D, E and F. Refer to the following legend to identify which sample is which:

Table 4.1: Crude Oil samples' legend

Sample	Label
Crude Oil	**A**
Crude Oil + Biopolymer	**B**
Crude Oil + 3% Drilling Mud	**C**
Crude Oil + 3% Drilling Mud + Biopolymer	**D**
Crude Oil + 9% Drilling Mud	**E**
Crude Oil + 9% Drilling Mud + Biopolymer	**F**

4.1. Wax Appearance Temperature

There are many parameters that can be observed in order to identify the wax appearance temperature of a sample. Using rheometer, wax appearance temperature can be determined from the sudden change in G' values, G" values and the raw phase (degree) values. Wax appearance temperature can also be determined from the increase in the viscosity values of the sample as it is cooled.

Sample A

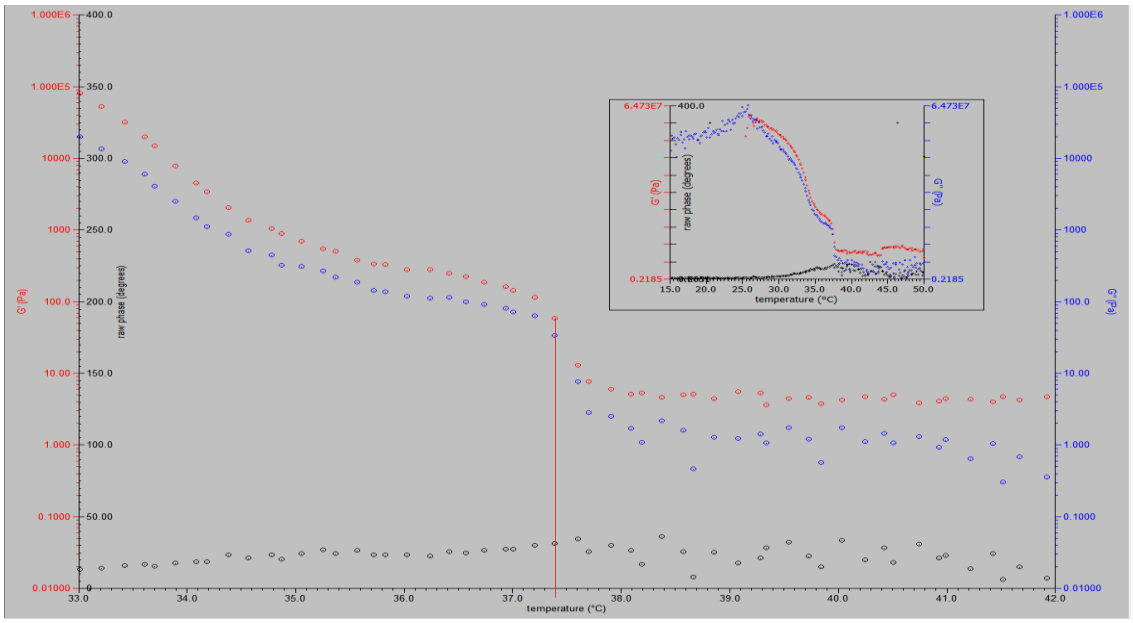


Figure 4.1: G', G" and raw phase against temperature of Sample A

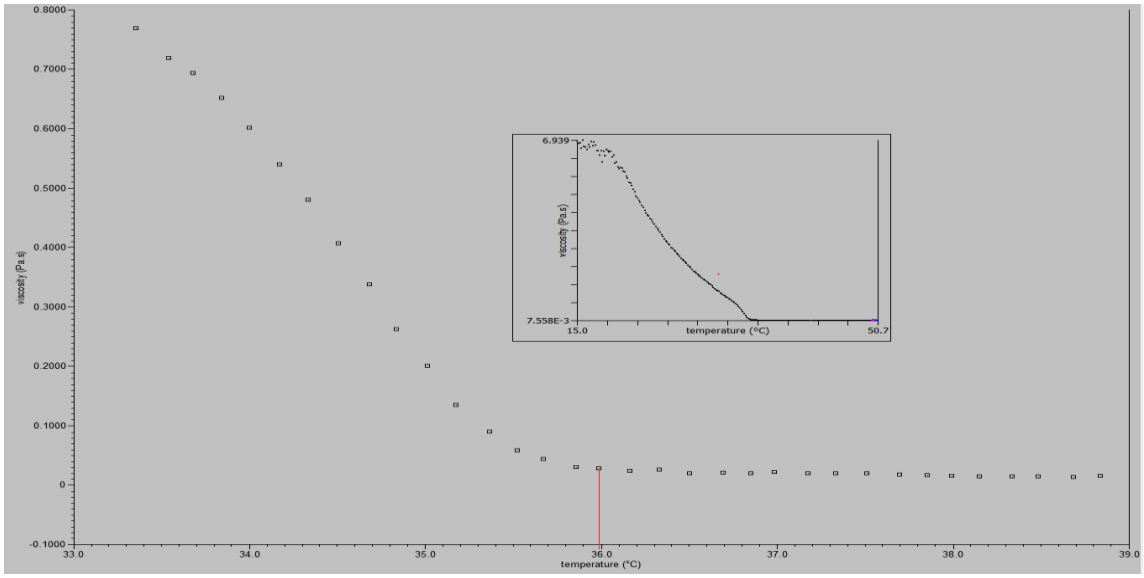


Figure 4.2: Viscosity against Temperature of Sample A

From Figure 4.1 it can be seen that Sample A have a wax appearance temperature of 37.4°C while Figure 4.2 gives a WAT of 36°C. Based on G' and G", the sudden increase in value indicate the formation of crystal structure. While referring to the viscosity, increases in viscosity above the average viscosity level indicate the formation of crystal.

Sample B

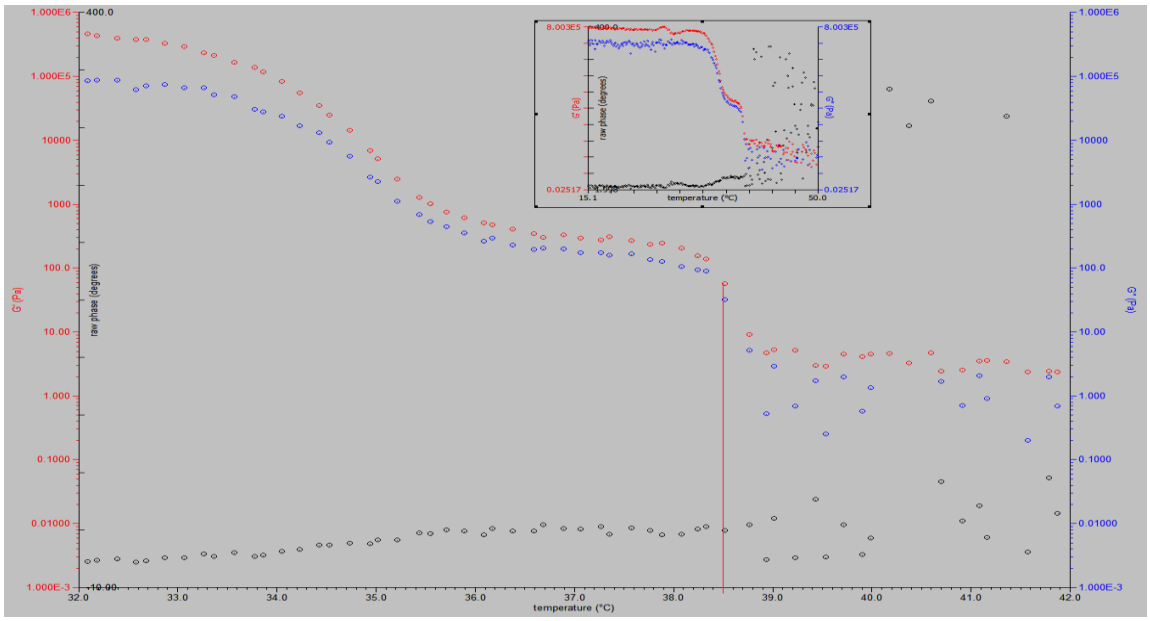


Figure 4.3: G', G" and raw phase against temperature of Sample B

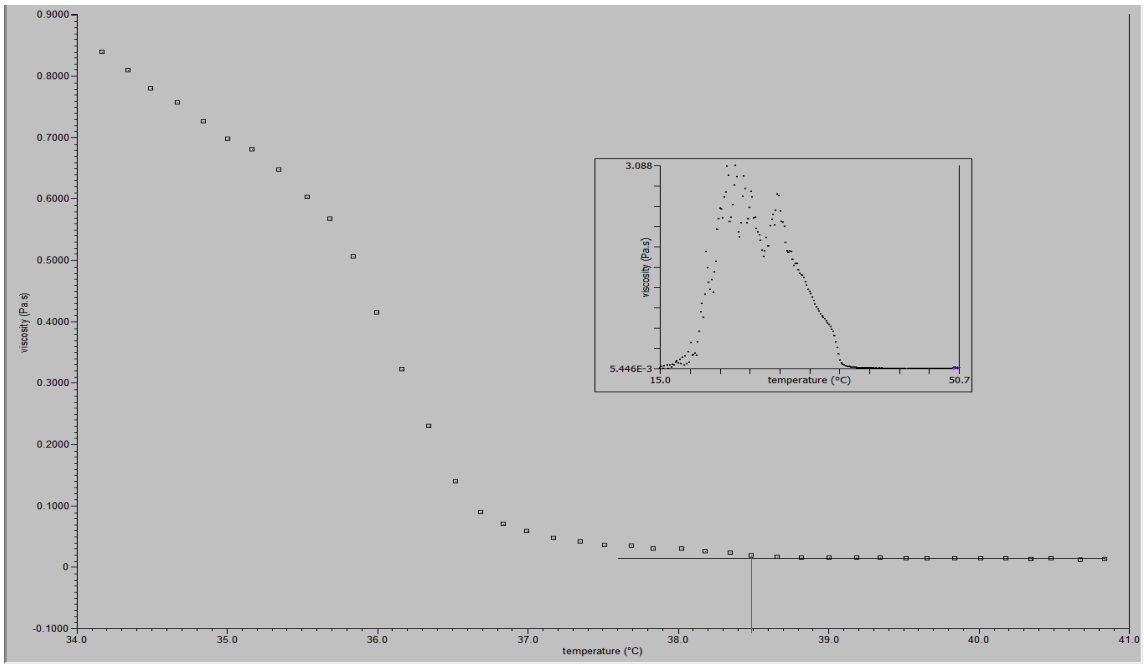


Figure 4.4: Viscosity against Temperature of Sample B

Figure 4.3 shows that sudden increase in G' and G" is at 38.5°C and Figure 4.4 also shows the increase of viscosity at 38.5°C. This concluded that Sample B has a wax appearance temperature of 38.5°C

Sample C

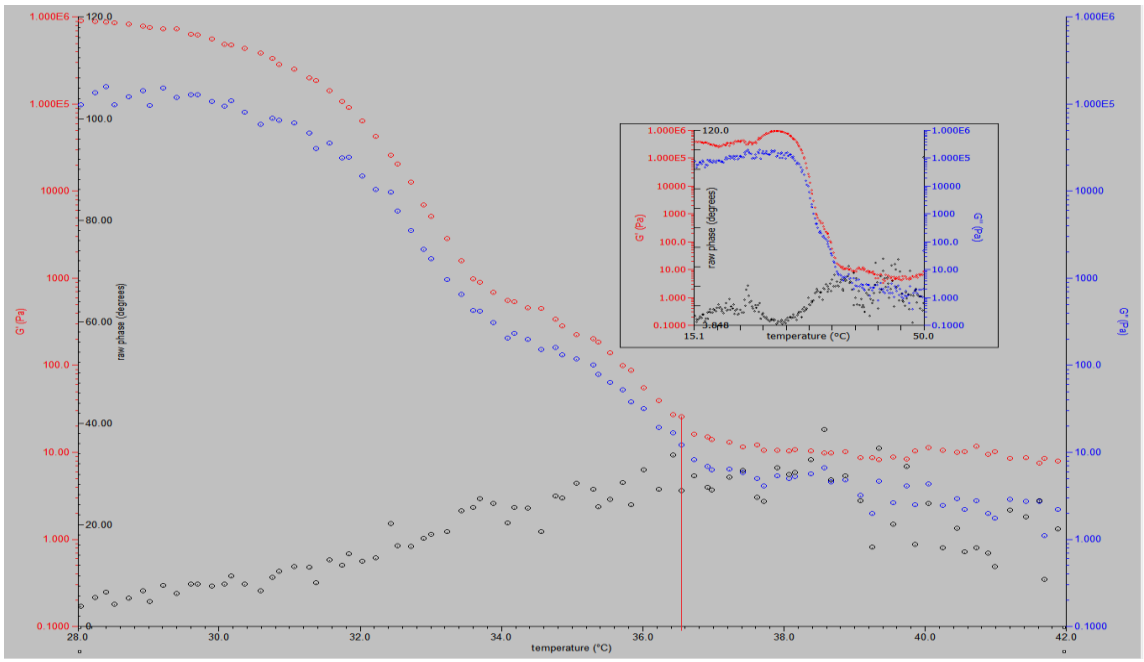


Figure 4.5: G', G" and raw phase against temperature of Sample C

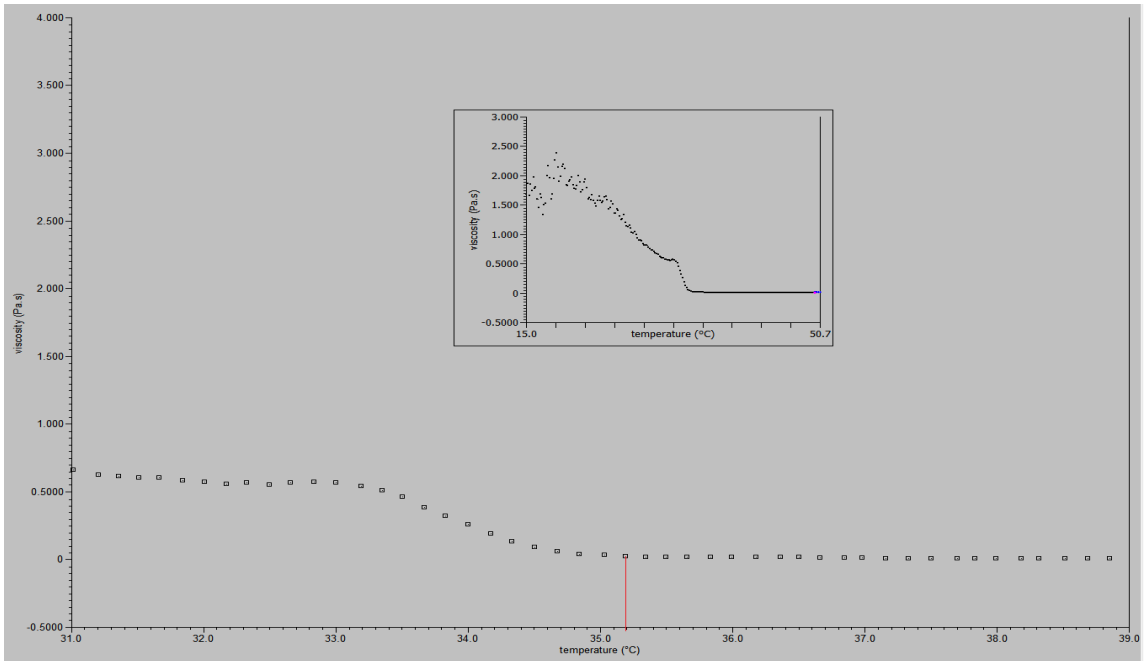


Figure 4.6: Viscosity against Temperature of Sample C

From Figure 4.5 it can be seen that Sample C has a wax appearance temperature of 36.3°C while Figure 4.6 gives a WAT of 35.2°C.

Sample D

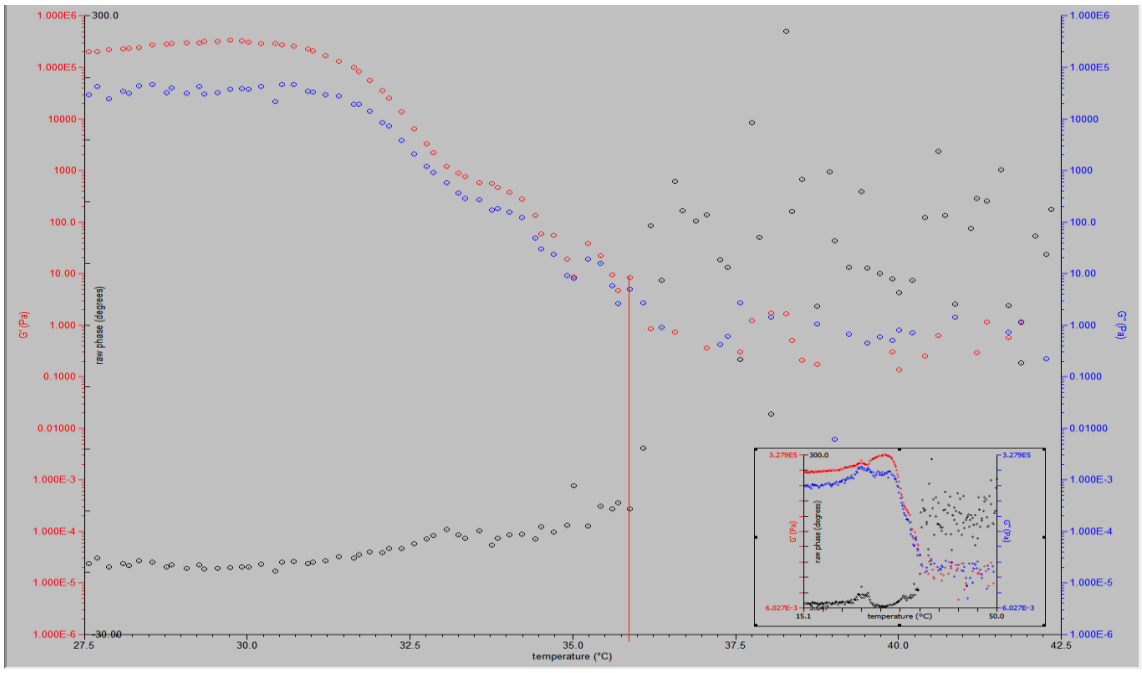


Figure 4.7: G', G" and raw phase against temperature of Sample D

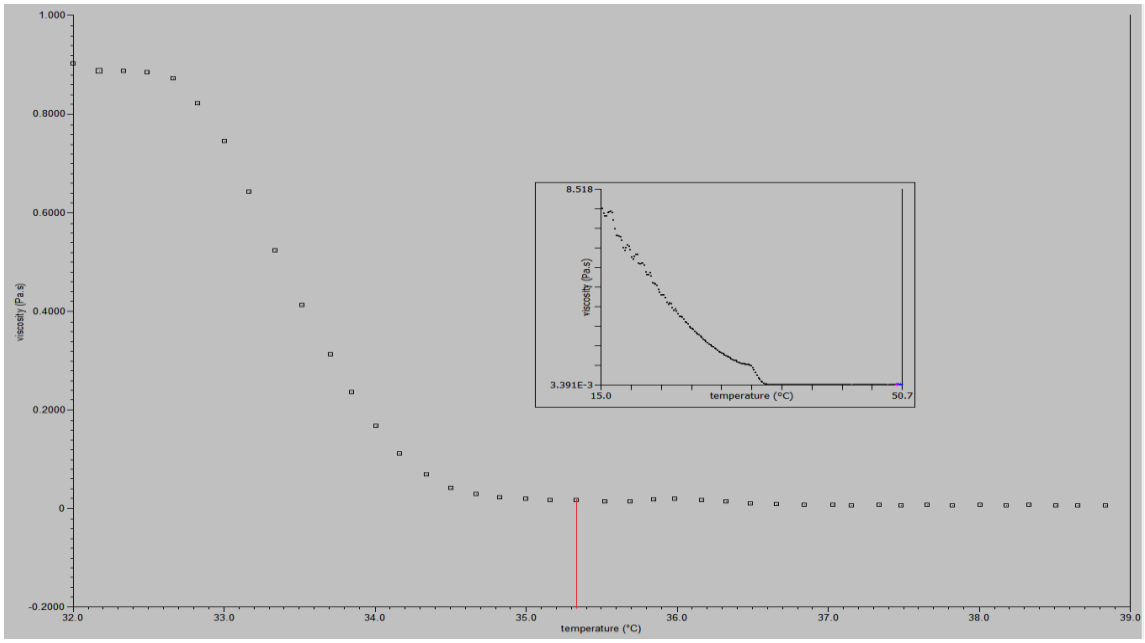


Figure 4.8: Viscosity against Temperature of Sample D

From Figure 4.7, the graphs indicates that the sudden increase in G' and G" started at 35.88°C while the viscosity graph indicate crystal formation at 35.3°C.

Sample E

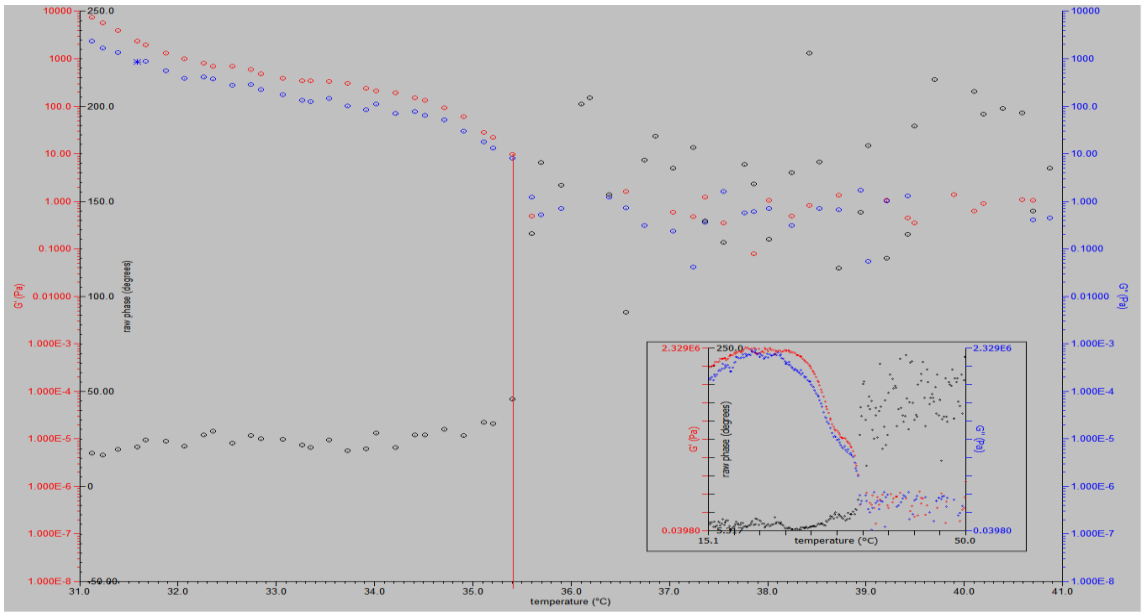


Figure 4.9: G', G" and raw phase against temperature of Sample E

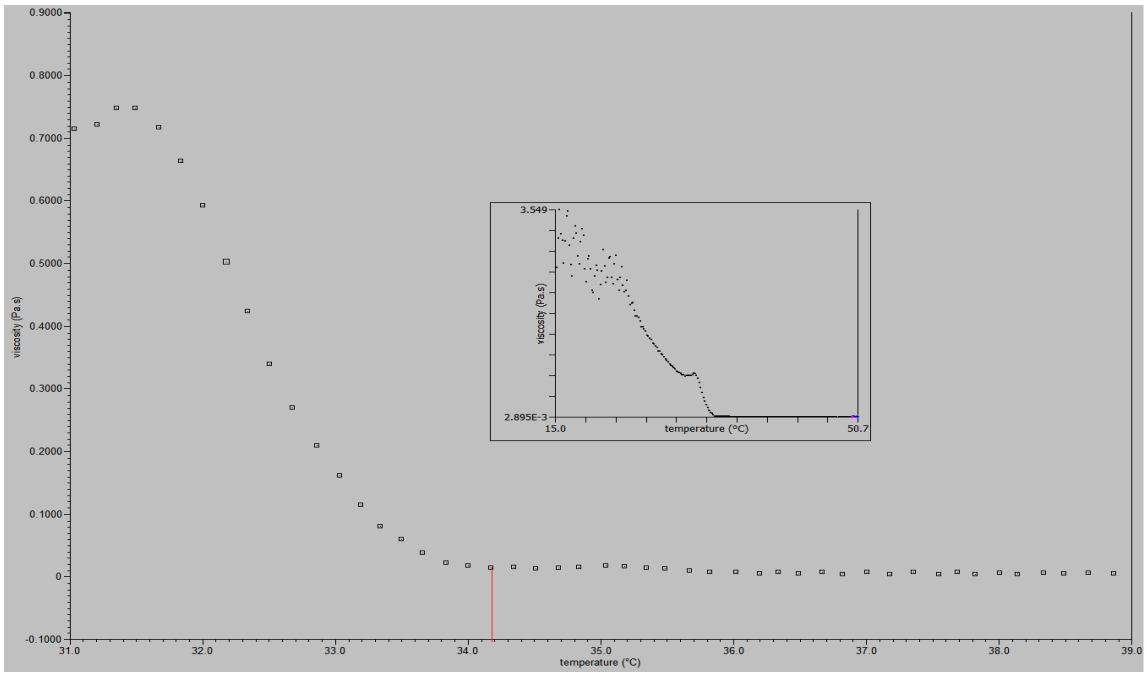


Figure 4.10: Viscosity against Temperature of Sample E

For sample E, Figure 4.9 indicate the wax appearance temperature of 35.4°C while Figure 4.10 at 34.2°C.

Sample F

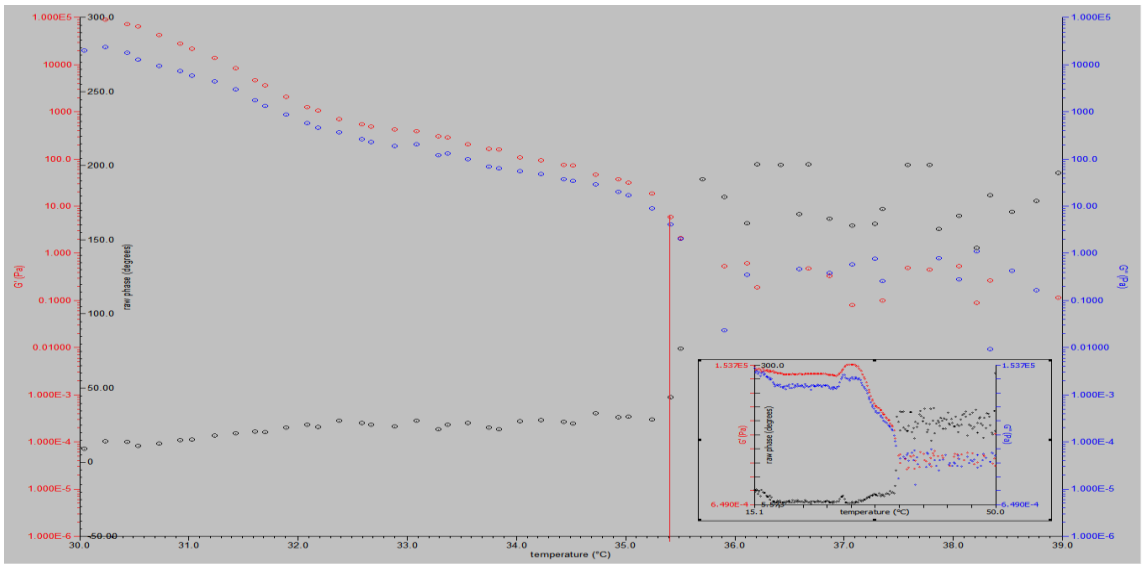


Figure 4.11: G', G" and raw phase against temperature of Sample F

:

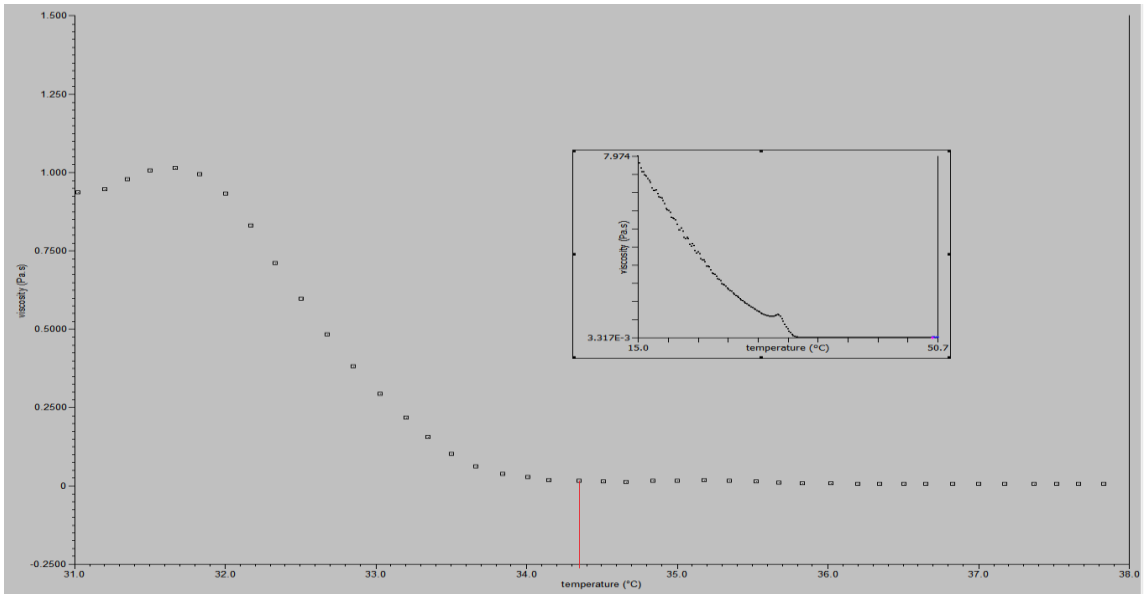


Figure 4.12: Viscosity against Temperature of Sample F

From Figure 4.11, the wax appearance temperature of Sample F is 35.4°C while Figure 4.12 shows 34.3°C as the wax appearance temperature.

As seen from these figures, it is easier to detect the sudden increase in the measured data that represent WAT on viscosity data plot than detecting the sudden increase in G',G" plots.

Table 4.2: Wax appearance temperature of Sample A, B, C, D, E and F

Sample	Wax Appearance Temperature	
	G' and G" against temperature, °C	Viscosity against temperature, °C
Crude Oil	37.40	36.00
Crude Oil + Biopolymer	38.50	38.50
Crude Oil + 3% Drilling Mud	36.30	35.20
Crude Oil + 3% Drilling Mud + Biopolymer	35.88	35.30
Crude Oil + 9% Drilling Mud	35.40	34.20
Crude Oil + 9% Drilling Mud + Biopolymer	35.40	34.30

Due to high believability of WAT data from the viscosity curves, these WAT will be used onwards. Figure 4.13 below is used to better illustrate the effects of adding into crude oil on one of the characteristics of crude oil; wax appearance temperature.

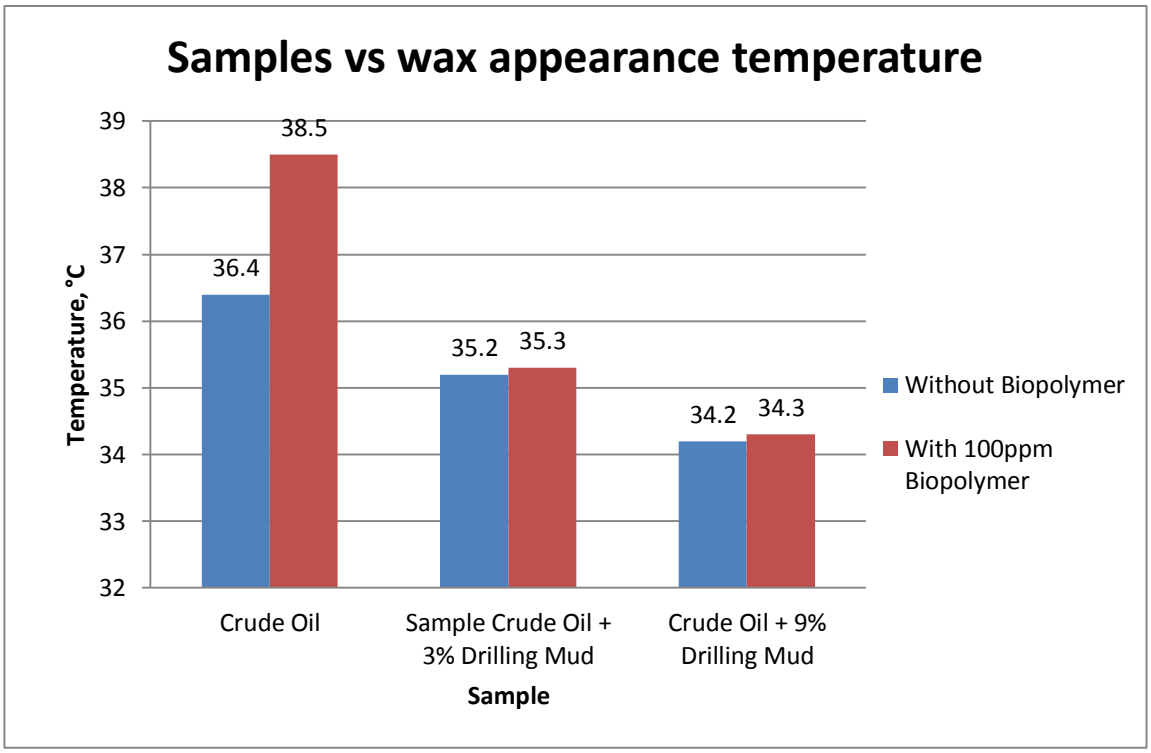


Figure 4.13: Comparison between samples with and without added biopolymer and their wax appearance temperature

From Figure 4.13 it can be observed that biopolymer has minimal effect on the WAT in the presence of DM. While the addition of DM reduces the WAT, the addition of biopolymer to "pare" crude oil increases the WAT.

4.2. Pour Point Test

Following are the results of pour point test on the samples.

Table 4.3: Pour point of Sample A, B, C, D, E and F

Sample	Temperature, **°C**
Crude Oil	**36**
Crude Oil + Biopolymer	**38**
Crude Oil + 3% Drilling Mud	**33**
Crude Oil + 3% Drilling Mud + Biopolymer	**34**
Crude Oil + 9% Drilling Mud	**32**
Crude Oil + 9% Drilling Mud + Biopolymer	**33**

Figure 4.14 below is used to better illustrate the effects of adding into crude oil on one of the characteristics of crude oil; pour point temperature.

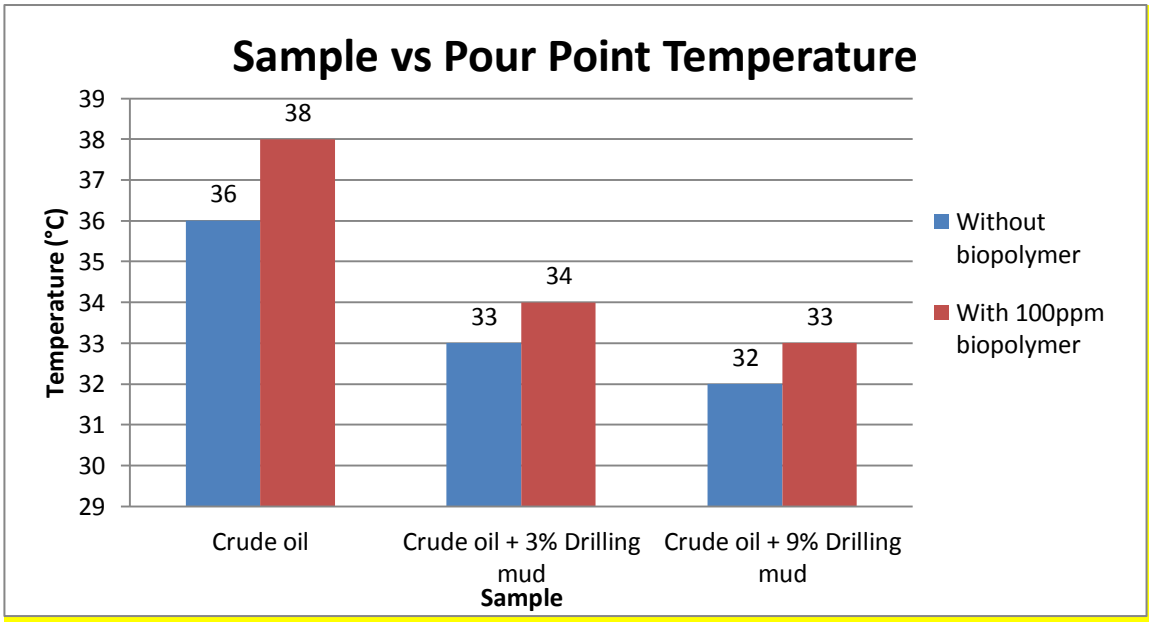


Figure 4.14 : Pour point temperature of different samples with and without biopolymer

From the above figure, the same trend in WAT can be seen in pour point. Addition of drilling mud reduced the pour point of the sample however the addition of biopolymer increases the pour point of the samples.

4.3. Carbon number distribution

Sample A and Sample B

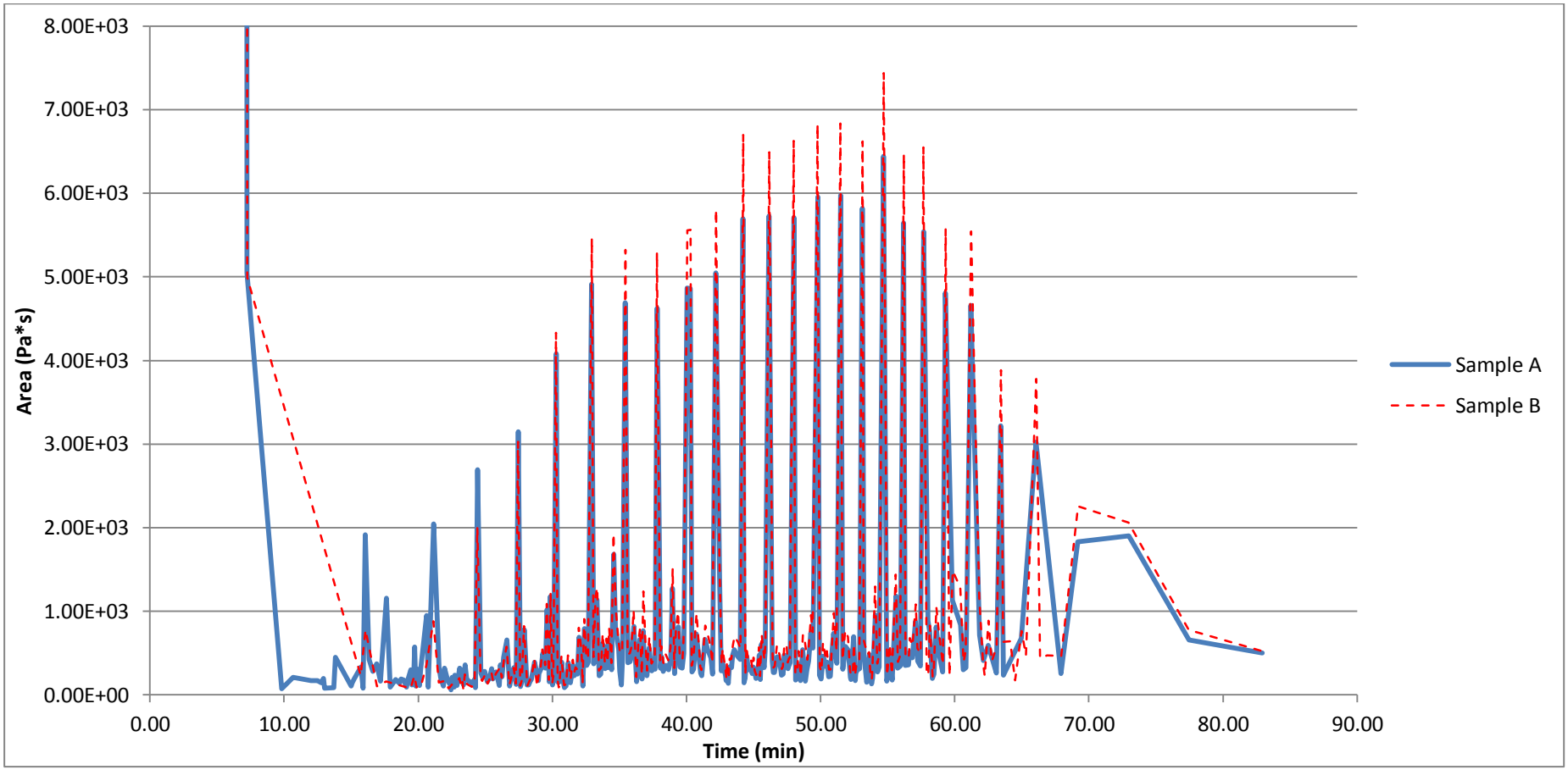


Figure 4.15 : Chromatogram of sample A and B

Sample C and Sample D

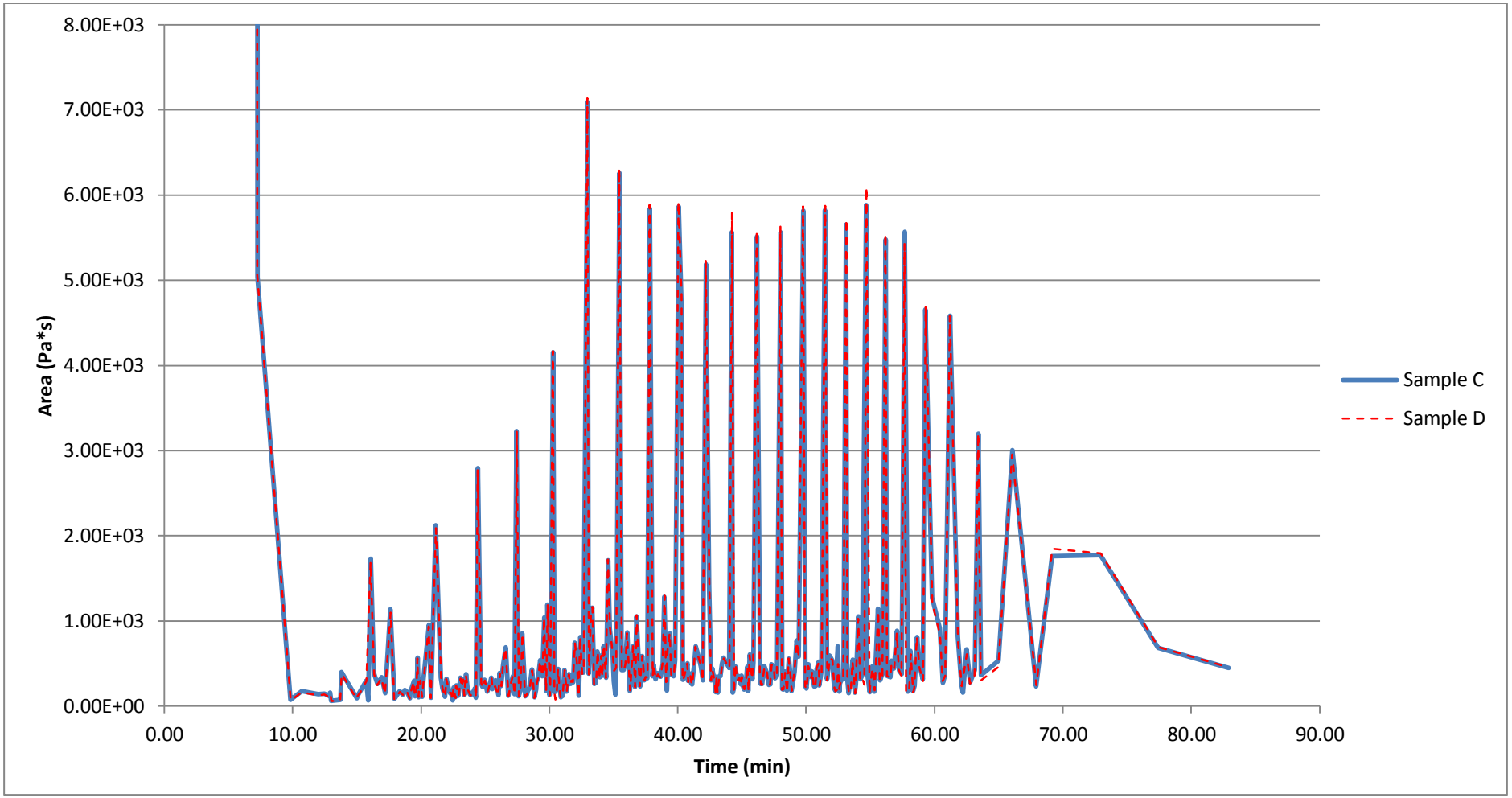


Figure 4.16 : Chromatogram of sample C and D

Sample E and F

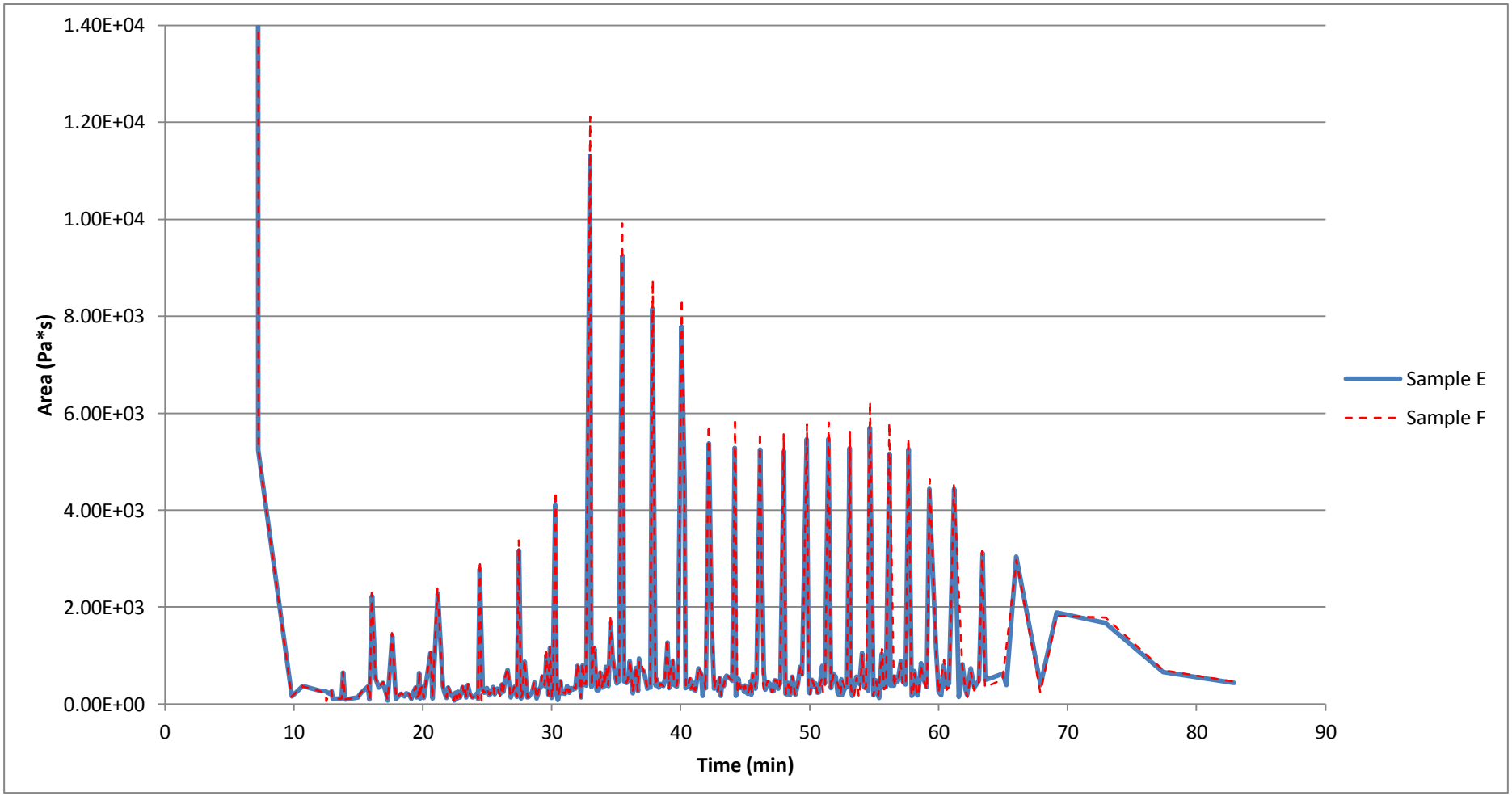


Figure 4.17 : Chromatogram of Sample E and F

Lower carbon number compounds will have lower boiling point compared to the higher carbon number compounds. This is due to stronger Van Der Waals force of attraction in higher carbon number compound. Thus it can be seen that the left most peak in the graph is the lowest carbon number compound and carbon number increases to the right.

As stated before, the samples were first diluted with hydrocarbon based solution. The solution used was Hexane. This explains the peak near the 10-minute marks.

From Figure 4.15, the addition of biopolymer causes the amount of compounds between 30-minute to 70-minute window to increase significantly. However, the amount of compounds outside this window experience small change.

Unlike in Figure 4.15, from Figure 4.16 it can be observed that there is almost no change in the amount of compound even with the addition of biopolymer. This trend can be seen throughout the whole test from 0-minute mark until the 83-minute point.

Figure 4.17 also shows the same trend as in Figure 4.15; increase in the amount of compounds, but at a smaller margin. This trend can be seen from 20 minutes to 60 minutes window.

It is probable that the carbon number of the compounds that increase with the addition of biopolymer ranging from C_{14} to C_{40} as these represents the waxy part of the crude oil, thus justify the increase in the wax appearance temperature and the pour point of the crude oil.

4.4. Limitation

4.4.1. Wax appearance temperature

During the cooling step of the sample, shrinkage of the crude oil might occur. This might causes loss of contact between the sample and the geometry and causes the errors in the results.

4.4.2. Pour point temperature

For pour point temperature, the results using the tilt method are only accurate up to 1°C. Due to this accuracy level, we are not able to determine the exact pour point of the sample. For example, Sample A has a pour point of 36°C, however it is not clear that at which point between 36°C and 37°C the sample started to stop behaving like a fluid.

4.4.3. Carbon number distribution

Using Gas Chromatography to determine the carbon number distribution has its limitation. Without preparing the standards before the test, the chromatograms will only shows the retention time of compounds and the amount of each compound. It, however, couldn't identify the carbon number of the compounds due to absence of standard and library that is required to determine the carbon number of each peak.

Furthermore, the standards and the samples should be run using the same column, parameter and system in order for us to be able to identify the carbon number for each peak. Without fulfilling these conditions, the results will be inaccurate and we wouldn't be able to identify the compounds.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1. Conclusion

In a nut shell, this project is a research to study the effects of biopolymer as drag reducing agent to the characteristics of crude oil. The characteristics to be studied are wax appearance temperature, pour point temperature and carbon number distribution.

From the results, it can be seen that adding biopolymer will slightly increases the wax appearance temperature of the crude oil. It is proven that biopolymer affects the crude oil by increasing the WAT.

The results also show that adding biopolymer will also affects the pour point of the crude oil. The same trend occurs in pour point as in the WAT where addition of biopolymer causes increase in pour point.

Adding biopolymer has effects on the carbon number distribution. Majority of the compounds increases with the addition biopolymer but this happens at different margin for different samples.

It is hoped that more research on how biopolymer affects the crude oil can be conducted as it would bring lots of benefit not only to oil and gas field but many other fields too.

5.2. Recommendation

Despites the completion of this project, the research on the effects of biopolymer as drag reducing agent on the characteristics of crude oil should be further extends. There are several recommendations that can be considered for future planning. The first is to study the effects of biopolymer on the wax disappearance temperature of crude oil. This is to simulate the flow of crude oil from colder region to a higher temperature region.

The second recommendation is to conduct the pour point test using pour point tester as it will give a better and more accurate reading up to one decimal place unlike the tilt method with the accuracy of only 1°C.

The last is to extend the study on the carbon number distribution. Instead of using Gas Chromatography, Gas Chromatography with Mass Spectrometry (GC/MS) can be used to run the samples and get the carbon number distribution without the need to prepare the standards. Each component can be identified by matching the molecular weight of the compound with the software's library. High Temperature Gas Chromatography (HTGC) can also be used in order to extend the range of the temperature operation so that more compounds in the sample can be identified.

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